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Columnar self-assembly, electrochemical and luminescent properties of basket shaped liquid crystalline derivatives of schiff base moulded p-*tert*-butylcalix[4]arene

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1. Synthesis and Characterization

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. The reference electrode was calibrated with the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple (absolute energy level of – 4.80 eV to vacuum).

Preparation of p-*tert*-butylcalix[4]arene (1a)

p-tert-butylcalix[4]arene (**1a**) was synthesized by reported method 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.

Preparation of p-*tert*-butylcalix[4]arene tetra-propionic acid (2a)

p-*tert*-butylcalix[4]arene tetra-propionic acid (**2a**) is prepared by the condensation reaction of compound **(1a)** with bromo propionic acid in dry acetone with presence of anhydrous K_2CO_3 as a base.[2] White precipitates, yield 73%. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.31 (s, 36H), 2.53 (t, 8H), 3.64 (s, 4H), 4.17 (t, 8H, *J* = 6.0Hz), 6.84 (s, 4H), 7.64 (s, 4H, *J* = 8.0Hz), 8.42 (s, 2H), 10.5 (s, 4H, -COOH); ^{13}C NMR: 160.6, 156.6, 144.7, 136.4, 122.5, 77.4, 77.4, 67.1, 35.2.

Preparation of 3,4-dibutyloxy benzaldehyde (3a)

3,4-dibutyloxy benzaldehyde (**3a**) was synthesized by refluxing the reaction mixture of 3,4-dihydroxy benzaldehyde (1 equiv.) with butyl bromide (2 equiv.) and anhydrous K_2CO_3 (2 equiv.) in dry acetone for 2 hr.[3] Yield 86 %, FT-IR (KBr) in cm^{-1}: 2976, 2860, 1664, 1234, 876, 771. ^{1}H NMR $CDCl_3$ (400 MHz): 0.89 (t, 6H, CH_3), 1.71 (p, 4H, CH_2), 4.06 (t, 4H, CH_2), 7.10 (s, 2H, Ar), 10.03 (s, 1H, CHO). ^{13}C NMR: 177.6, 164.1, 144.6, 108.1, 77.8, 31.4, 29.8, 22.7.

Preparation of 3,4-dioctyloxy benzaldehyde (3b)

3,4-dioctyloxy benzaldehyde (**3b**) was synthesized by refluxing the reaction mixture of 3,4-dihydroxy benzaldehyde (1 equiv.) with octyl bromide (2 equiv.) and anhydrous K_2CO_3 (2 equiv.) in dry acetone for 2 hr.[3] Yield 82 %, FT-IR (KBr) in cm^{-1}: 2943, 2801, 1660, 1234, 872, 776, 663. ^{1}H NMR $CDCl_3$ (400 MHz): 0.89 (t, 6H, CH_3), 1.26-1.47 (m, 8H, CH_2), 1.71 (p, 4H, CH_2), 4.06 (t, 4H, CH_2), 7.10 (s, 2H, Ar), 10.03 (s, 1H, CHO). ^{13}C NMR: 177.6, 164.1, 144.6, 141.5, 108.1, 77.8, 31.4, 29.8, 22.7, 19.4.

Preparation of 3,4-didoceyloxy benzaldehyde (3c)

3,4-didodecyloxy benzaldehyde (**3c**) was synthesized by refluxing the reaction mixture of 3,4-dihydroxy benzaldehyde (1 equiv.) with dodecyl bromide (2 equiv.) and anhydrous K_2CO_3 (2 equiv.) in dry acetone for 2 hr.[3] Yield 74 %, FT-IR (KBr) in cm^{-1}: 2915, 2867, 1640, 1440, 1212, 1121, 821, 756, 663, 632. ^{1}H NMR $CDCl_3$ (400 MHz): 0.89 (t, 6H, CH_3), 1.26-1.47 (m, 28 H, CH_2), 1.71 (p, 4H, CH_2), 4.08 (t, 4H, CH_2), 7.34 (s, 2H, Ar), 10.06 (s, 1H, CHO). ^{13}C NMR: 177.6, 164.1, 144.6, 141.5, 108.1, 77.8, 31.4, 29.8, 22.7, 19.4.

Preparation of 3,4-ditetradecyloxy benzaldehyde (3d)

3,4-ditetradecyloxy benzaldehyde (**3d**) was synthesized by refluxing the reaction mixture of 3,4-dihydroxy benzaldehyde (1 equiv.) with tetradecyl bromide (2 equiv.) and anhydrous K_2CO_3 (2 equiv.) in dry acetone for 2 hr.[3] Yield 78 %, FT-IR (KBr) in cm^{-1}: 2940, 2808, 1630, 1441, 1210, 1121, 892, 752, 676, 630. ^{1}H NMR $CDCl_3$ (400 MHz): 0.89 (t, 6H, CH_3), 1.26-1.47 (m, 34 H, CH_2), 1.73 (p, 4H, CH_2), 4.08 (t, 4H, CH_2), 7.34 (s, 2H, Ar), 10.06 (s, 1H, CHO). ^{13}C NMR: 173.6, 164.1, 144.6, 141.4, 108.1, 77.8, 31.8, 29.8, 22.7, 19.6.

Preparation of 4-((3,4-dibutyloxy benzylidene) amino) phenol (4a)

4-((3,4-dibutyloxy benzylidene) amino) phenol **(4a)** was synthesized by refluxing the reaction mixture of compound (**3a**) (1 equiv.) with 4-amino phenol (1 equiv.) in ethanol with presence of few drops of acetic acid for 3 hr.[4] The obtained crude product is further purified by column chromatography using (3:2) ratio of ethyl acetate and hexane. Yield 72%, FT-IR (KBr) in cm^{-1}: 2976, 2860, 1404, 1214, 1124, 876, 762. ^{1}H NMR $CDCl_3$ (400 MHz): 0.88 (t, 6H, CH_3), 1.71 (p, 4H, CH_2), 4.06 (t, 4H, CH_2), 5.12 (s, 1H, -OH), 6.82 (d, 2H, Ar, J = 6.0 Hz), 7.10 (d, 2H, Ar, J =

6.1 Hz), 7.42 (d, 2H, Ar), 8.21 (s, 1H, -CH=N). ^{13}C NMR: 160.1, 144.6, 124.1, 122.5, 108.1, 77.8, 68.7, 31.4, 29.8, 22.7.

Preparation of 4-((3,4-dioctyloxy benzylidene) amino) phenol (4b)

4-((3,4-dioctyloxy benzylidene) amino) phenol **(4b)** was synthesized by refluxing the reaction mixture of compound (**3b**) (1 equiv.) with 4-amino phenol (1 equiv.) in ethanol with presence of few drops of acetic acid for 3 hr.[4] The obtained crude product is further purified by column chromatography using (3:2) ratio of ethyl acetate and hexane. Yield 71%, FT-IR (KBr) in cm^{-1}: 2970, 2803, 1440, 1210, 1123, 870, 782, 661. ^{1}H NMR $CDCl_3$ (400 MHz): 0.88 (t, 6H, CH_3), 1.26 (m, 8H, CH_2), 1.73 (p, 4H, CH_2), 4.04 (t, 4H, CH_2), 5.10 (s, 1H, -OH), 6.86 (d, 2H, Ar, J = 6.1 Hz), 7.10 (d, 2H, Ar, J = 6.2 Hz), 7.43 (d, 2H, Ar), 8.18 (s, 1H, -CH=N). ^{13}C NMR: 160.1, 144.6, 141.2, 124.1, 122.5, 108.1, 77.8, 68.7, 31.4, 29.8, 22.6.

Preparation of 4-((3,4-didodecyloxy benzylidene) amino) phenol (4c)

4-((3,4-didodecyloxy benzylidene) amino) phenol **(4c)** was synthesized by refluxing the reaction mixture of compound (**3c**) (1 equiv.) with 4-amino phenol (1 equiv.) in ethanol with presence of few drops of acetic acid for 3 hr.[4] The obtained crude product is further purified by column chromatography using (3:2) ratio of ethyl acetate and hexane. Yield 72%, FT-IR (KBr) in cm^{-1}: 2976, 2860, 1404, 1214, 1124, 876, 762. ^{1}H NMR $CDCl_3$ (400 MHz): 0.88 (t, 6H, CH_3), 1.26-1.28 (m, 28H, CH_2), 1.73 (p, 4H, CH_2), 4.06 (t, 4H, CH_2), 5.02 (s, 1H, -OH), 6.88 (d, 2H, Ar, J = 6.2 Hz), 7.14 (d, 2H, Ar, J = 6.6 Hz), 7.51 (d, 2H, Ar), 8.14 (s, 1H, -CH=N). ^{13}C NMR: 160.1, 144.6, 124.1, 123.5, 110.3, 77.8, 66.7, 31.4, 29.8, 22.7.

Preparation of 4-((3,4-ditetradecyloxy benzylidene) amino) phenol (4d)

4-((3,4-ditetradecyloxy benzylidene) amino) phenol **(4d)** was synthesized by refluxing the reaction mixture of compound (**3d**) (1 equiv.) with 4-amino phenol (1 equiv.) in ethanol with

presence of few drops of acetic acid for 3 hr.[4] The obtained crude product is further purified by column chromatography using (3:2) ratio of ethyl acetate and hexane. Yield 76%, FT-IR (KBr) in cm^{-1}: 2906, 2830, 1410, 1234, 1124, 871, 740, 632, 592. ^{1}H NMR $CDCl_3$ (400 MHz): 0.88 (t, 6H, CH_3), 1.26-1.28 (m, 36H, CH_2), 1.73 (p, 4H, CH_2), 4.06 (t, 4H, CH_2), 5.12 (s, 1H, -OH), 6.78 (d, 2H, Ar, J = 6.4 Hz), 7.14 (d, 2H, Ar, J = 6.2 Hz), 7.41 (d, 2H, Ar), 8.23 (s, 1H, -CH=N). ^{13}C NMR: 160.1, 144.6, 141.4, 124.1, 122.5, 108.1, 77.8, 6.7, 31.4, 29.8, 22.7.

Preparation of p-*tert*-butylcalix[4]arene schiff-base ester tetra-butyloxy derivatives (5a)

p-*tert*-butylcalix[4]arene schiff-base ester tetra-butyloxy derivatives **(5a)** were prepared by the reaction of compound **(4a)** with compound **(2a)** by using EDC.HCl and DMAP as catalyst in dichloromethane for 24 hr at room temperature.[5] The resultant crude residue was purified by using column chromatography on silica gel eluting with methanol: chloroform (1:4, v/v) as the eluent. The tetra substitution on lower rim of calixarene core was ascertained by the absence of –OH group from ^{1}H NMR and FT-IR study. Yield 66 %, FT-IR (KBr) in cm^{-1}: 2991, 2880, 1750, 1610, 1531, 1440, 1224, 1120, 980, 886. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (t, 24H, -OCH_3), 1.26 (m, 12H), 1.31 (s, 36H, t-butyl group), 1.43 (sext, 16H, CH_2), 1.71 (p, 16H, CH_2), 4.08 (t, 16H, CH_2), 3.28 (s, 4H, CH_2), 4.23 (s, 4H, CH_2), 2.56 (s, 8H, CH_2), 4.41 (s, 8H, CH_2), 7.14 (s, 2H, J = 6.0 Hz, Ar), 6.87 (s, 4H, J = 6.2 Hz, Ar), 7.47 (d, 6H, J = 6.3 Hz, Ar), 6.91 (d, 8H, Ar), 7.21 (s, 4H, Ar), 6.67 (d, 4H, J = 5.8 Hz, Ar), 7.38 (d, 6H, J = 6.4 Hz, Ar), 8.64 (s, 4H, -CH=N). ^{13}C NMR: 161.4, 144.7, 141.7, 128.6, 135.8, 131.6, 129.7, 127.6, 122.2, 117.4, 77.3, 69.1, 68.7, 35.2, 34.8, 31.8, 19.6, 14.2. MALDI Tof MS for compound **5a** (M+1) Calculated: 2260.3154 Found 2261.3241.

Preparation of p-*tert*-butylcalix[4]arene schiff-base ester tetra-octyloxy derivatives (5b)

p-*tert*-butylcalix[4]arene schiff-base ester tetra-octyloxy derivatives **(5b)** were prepared by the reaction of compound **(4b)** with compound **(2a)** by using EDC.HCl and DMAP as catalyst in dichloromethane for 24 hr at room temperature.[5] The resultant crude residue was purified by using column chromatography on silica gel eluting with methanol: chloroform (1:4, v/v) as the eluent. The tetra substitution on lower rim of calixarene core was ascertained by the absence of –OH group from ^{1}H NMR and FT-IR study. Yield 71 %, FT-IR (KBr) in cm^{-1}: 2990, 2803, 1740, 1620, 1530, 1430, 1220, 980, 882, 774. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (t, 24H, -OCH_3), 1.26 (m, 74H, CH_2), 1.31 (s, 36H, t-butyl group), 1.43 (sext, 16H, CH_2), 1.71 (p, 16H, CH_2), 4.08 (t, 16H, CH_2), 3.28 (s, 4H, CH_2), 4.23 (s, 4H, CH_2), 2.56 (s, 8H, CH_2), 4.40 (s, 8H, CH_2), 7.10 (s, 2H, *J* = 6.0 Hz, Ar), 6.70 (s, 4H, *J* = 6.0 Hz, Ar), 7.53 (d, 6H, *J* = 6.2 Hz, Ar), 6.93 (d, 8H, Ar), 7.21 (s, 4H, Ar), 6.67 (d, 4H, *J* = 5.8 Hz, Ar), 7.38 (d, 6H, *J* = 6.4 Hz, Ar), 8.63 (s, 4H, -CH=N). ^{13}C NMR: 160.4, 144.6, 141.7, 128.6, 137.2, 130.8, 129.7, 127.6, 122.2, 114.4, 77.3, 69.9, 34.8, 31.8, 19.6, 14.2. MALDI Tof MS for compound **5b** (M+1) Calculated: 2708.8136 Found 2709.9342.

Preparation of p-*tert*-butyl calix[4]arene schiff-base ester tetra-dodecyloxy derivatives (5c)

p-*tert*-butylcalix[4]arene schiff-base ester tetra-dodecyloxy derivatives **(5c)** were prepared by the reaction of compound **(4c)** with compound **(2a)** by using EDC.HCl and DMAP as catalyst in dichloromethane for 24 hr at room temperature.[5] The resultant crude residue was purified by using column chromatography on silica gel eluting with methanol: chloroform (1:4, v/v) as the eluent. The tetra substitution on lower rim of calixarene core was ascertained by the absence of –OH group from ^{1}H NMR and FT-IR study. Yield 62 %, FT-IR (KBr) in cm^{-1}: 2987, 2810, 1730, 1621, 1520, 1440, 980, 825, 774, 642. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (t, 24H, -OCH_3), 1.24-1.26 (m, 152H, CH_2), 1.31 (s, 36H, t-butyl group), 1.43 (sext, 16H, CH_2), 1.71 (p, 16H, CH_2),

4.04 (t, 16H, CH_2), 3.28 (s, 4H, CH_2), 4.21 (s, 4H, CH_2), 2.54 (s, 8H, CH_2), 4.40 (s, 8H, CH_2), 7.24 (s, 2H, *J* = 6.4 Hz, Ar), 6.64 (s, 4H, *J* = 6.1 Hz, Ar), 7.51 (d, 6H, *J* = 6.2 Hz, Ar), 7.14 (d, 8H, Ar), 7.21 (s, 4H, Ar), 6.72 (d, 4H, *J* = 6.1 Hz, Ar), 7.42 (d, 6H, *J* = 6.2 Hz, Ar), 8.59 (s, 4H, -CH=N). ^{13}C NMR: 160.4, 144.6, 140.7, 127.6, 137.2, 130.8, 129.7, 126.6, 122.2, 112.2, 77.3, 69.9, 34.8, 31.8, 19.6. MALDI Tof MS for compound **5c** (M+1) Calculated: 3158.3274 Found 3159.6324.

Preparation of p-*tert*-butyl calix[4]arene schiff-base ester tetra-tetradecyloxy derivatives (5d)

p-*tert*-butylcalix[4]arene schiff-base ester tetra-tetradecyloxy derivatives **(5d)** were prepared by the reaction of compound **(4d)** with compound **(2a)** by using EDC.HCl and DMAP as catalyst in dichloromethane for 24 hr at room temperature.[5] The resultant crude residue was purified by using column chromatography on silica gel eluting with methanol: chloroform (1:4, v/v) as the eluent. The tetra substitution on lower rim of calixarene core was ascertained by the absence of –OH group from ^{1}H NMR and FT-IR study. Yield 59 %, FT-IR (KBr) in cm^{-1}: 2904, 2896, 1740, 1620, 1513, 1430, 986, 820,774, 640. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (t, 24H, -OCH_3), 1.24-1.26 (m, 152H, CH_2), 1.31 (s, 36H, t-butyl group), 1.43 (sext, 16H, CH_2), 1.71 (p, 16H, CH_2), 4.04 (t, 16H, CH_2), 3.28 (s, 4H, CH_2), 4.21 (s, 4H, CH_2), 2.54 (s, 8H, CH_2), 4.40 (s, 8H, CH_2), 7.24 (s, 2H, *J* = 6.4 Hz, Ar), 6.62 (s, 4H, *J* = 6.1 Hz, Ar), 7.55 (d, 6H, *J* = 6.1 Hz, Ar), 7.10 (d, 8H, Ar), 7.21 (s, 4H, Ar), 6.73 (d, 4H, *J* = 6.4 Hz, Ar), 7.34 (d, 6H, *J* = 6.1 Hz, Ar), 8.61 (s, 4H, -CH=N). ^{13}C NMR: 160.4, 144.6, 140.7, 127.6, 137.2, 130.8, 129.7, 126.6, 122.2, 112.2, 77.3, 69.9, 34.8, 31.8, 19.6. MALDI Tof MS for compound **5d** (M+1) Calculated: 3382.6532 Found 3383.7648.

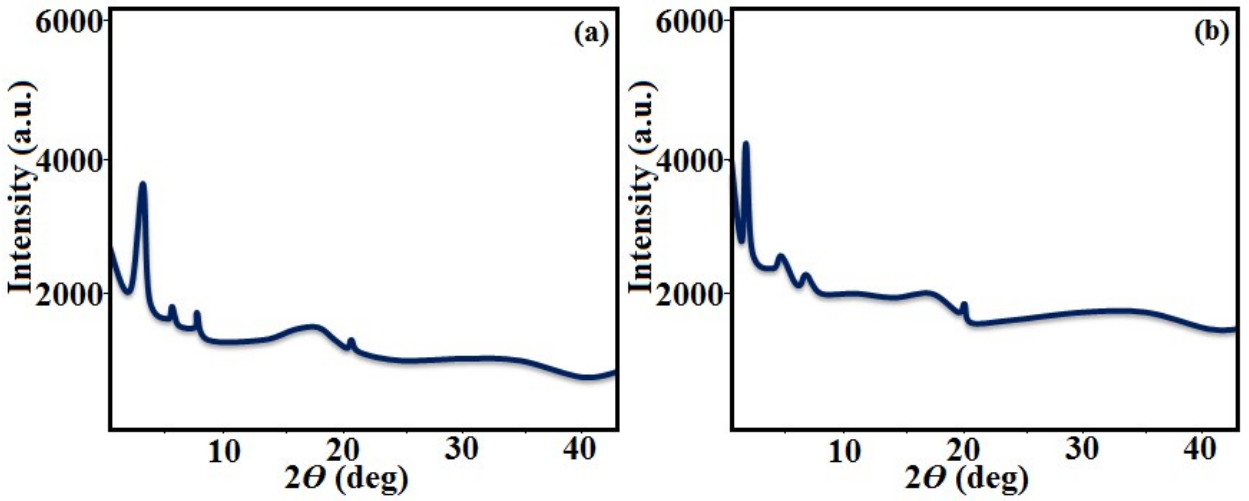

Figure S_1. XRD profiles depicting the intensity against the 2Θ obtained for the Col_h phase of compound **5b** at 84.0 ˚C (a); Col_h phase of compound **5d** at 61.0 ˚C (b) on cooling from isotropic temperature; the insert shows the image pattern obtained.

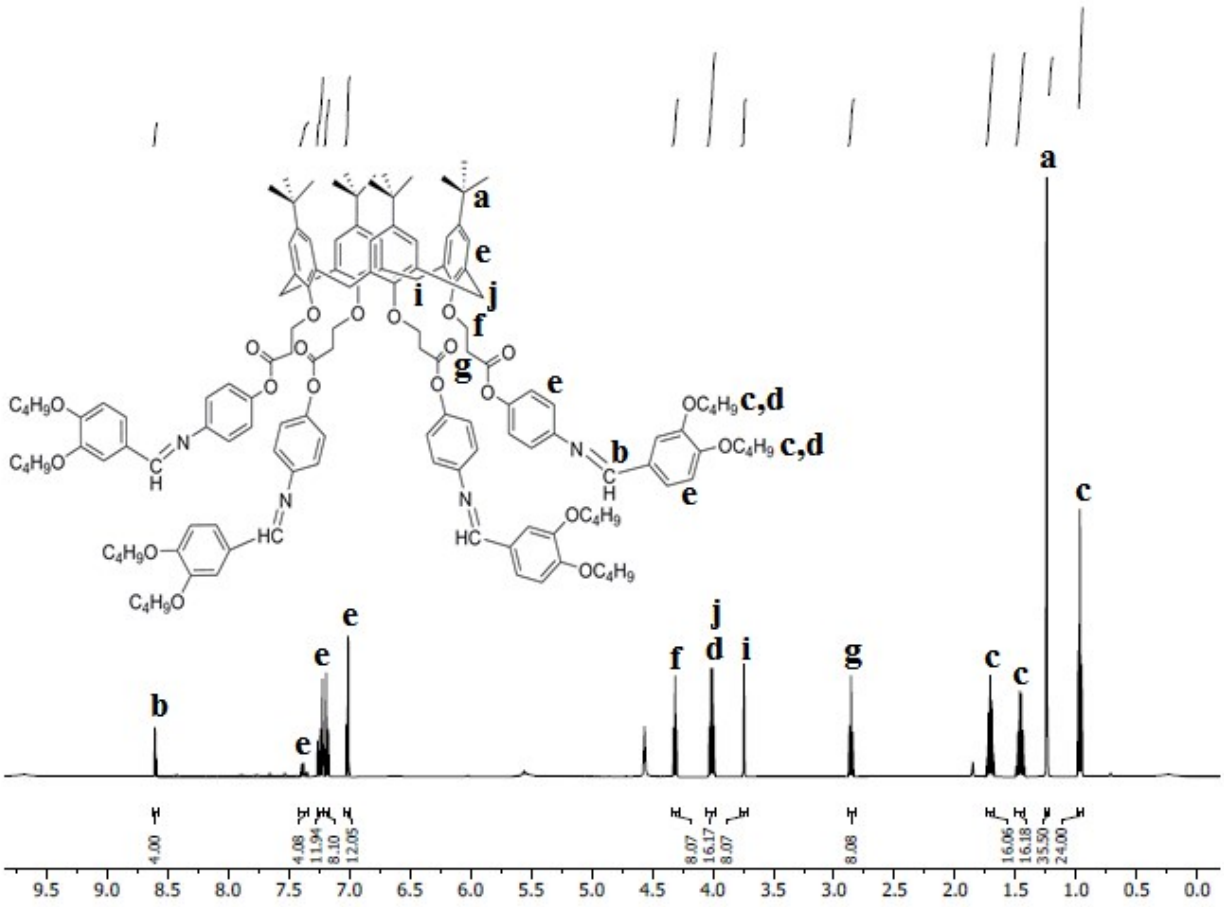

Figure S_2. ^{1}H NMR of compound **5a**

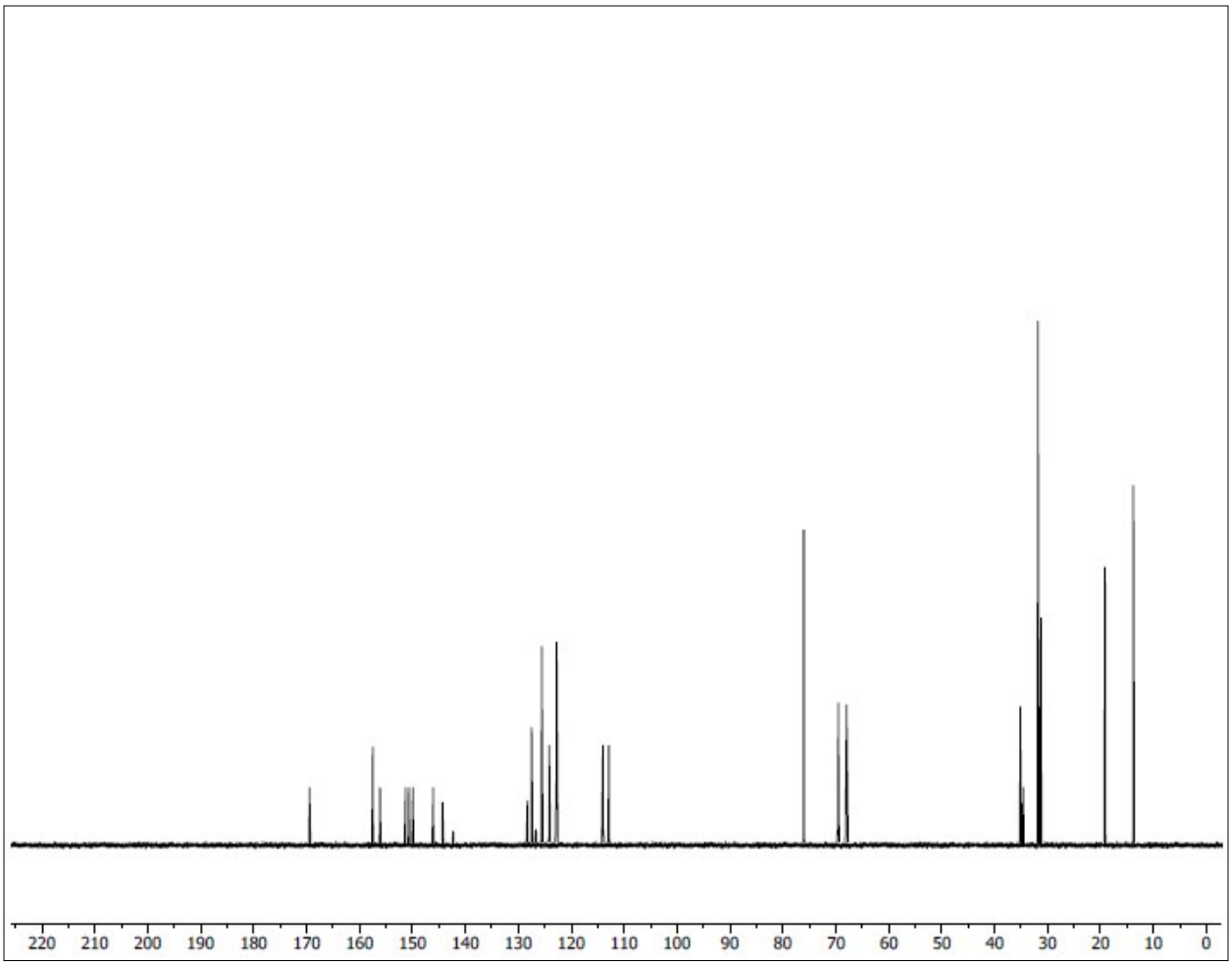

Figure S_3. ^{13}C NMR of compound **5a**

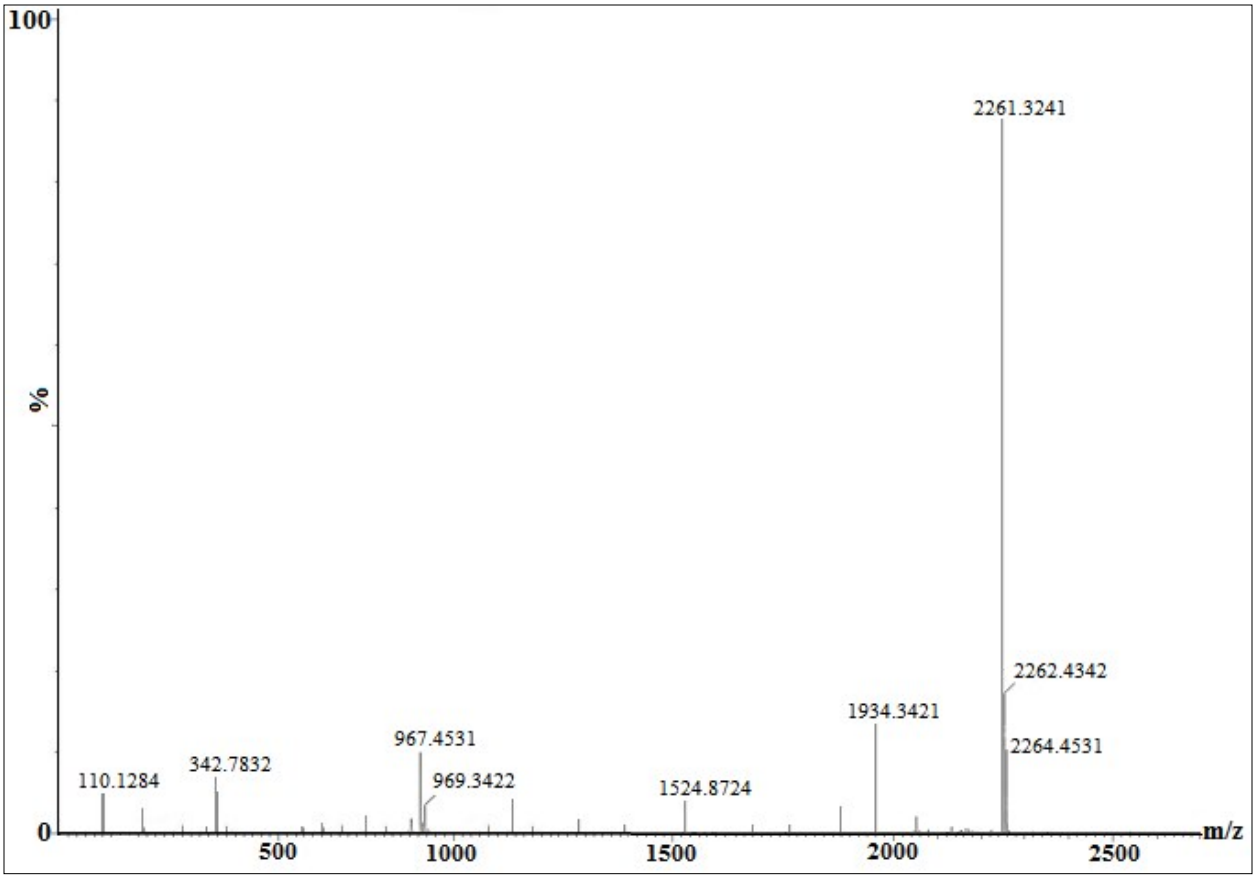

Figure S4. HRMS of compound **5a**

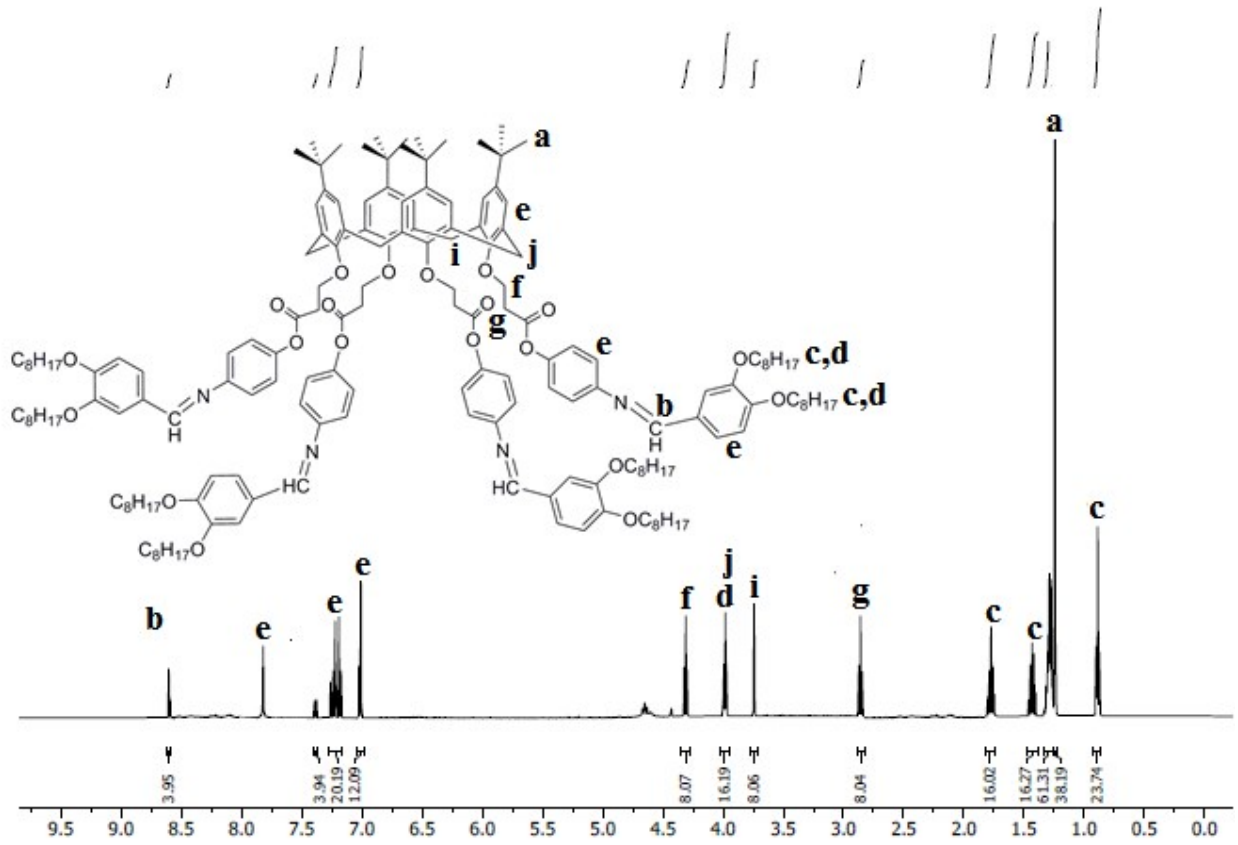

Figure S_5. ^{1}H NMR of compound **5b**

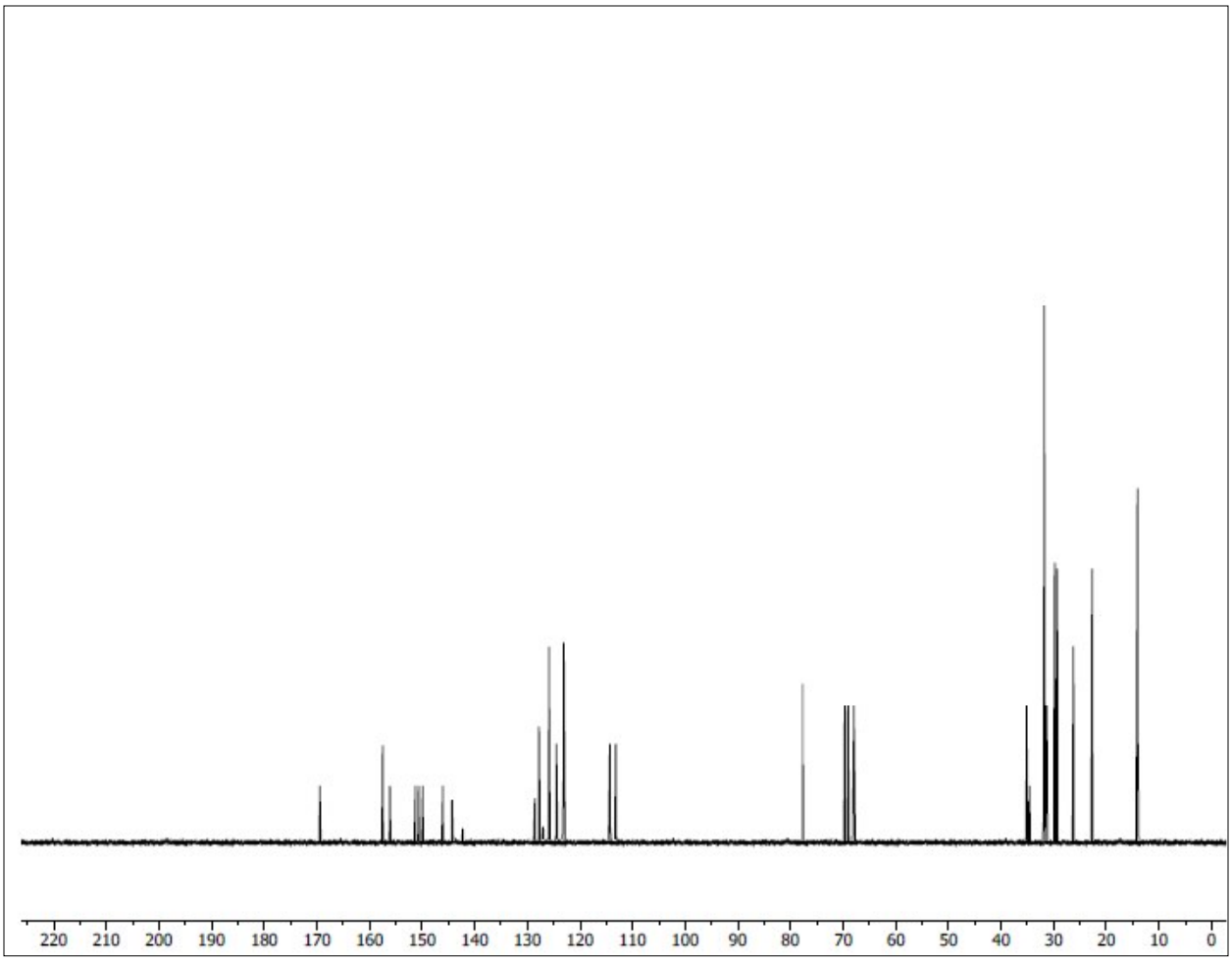

Figure S_6. ^{13}C NMR of compound **5b**

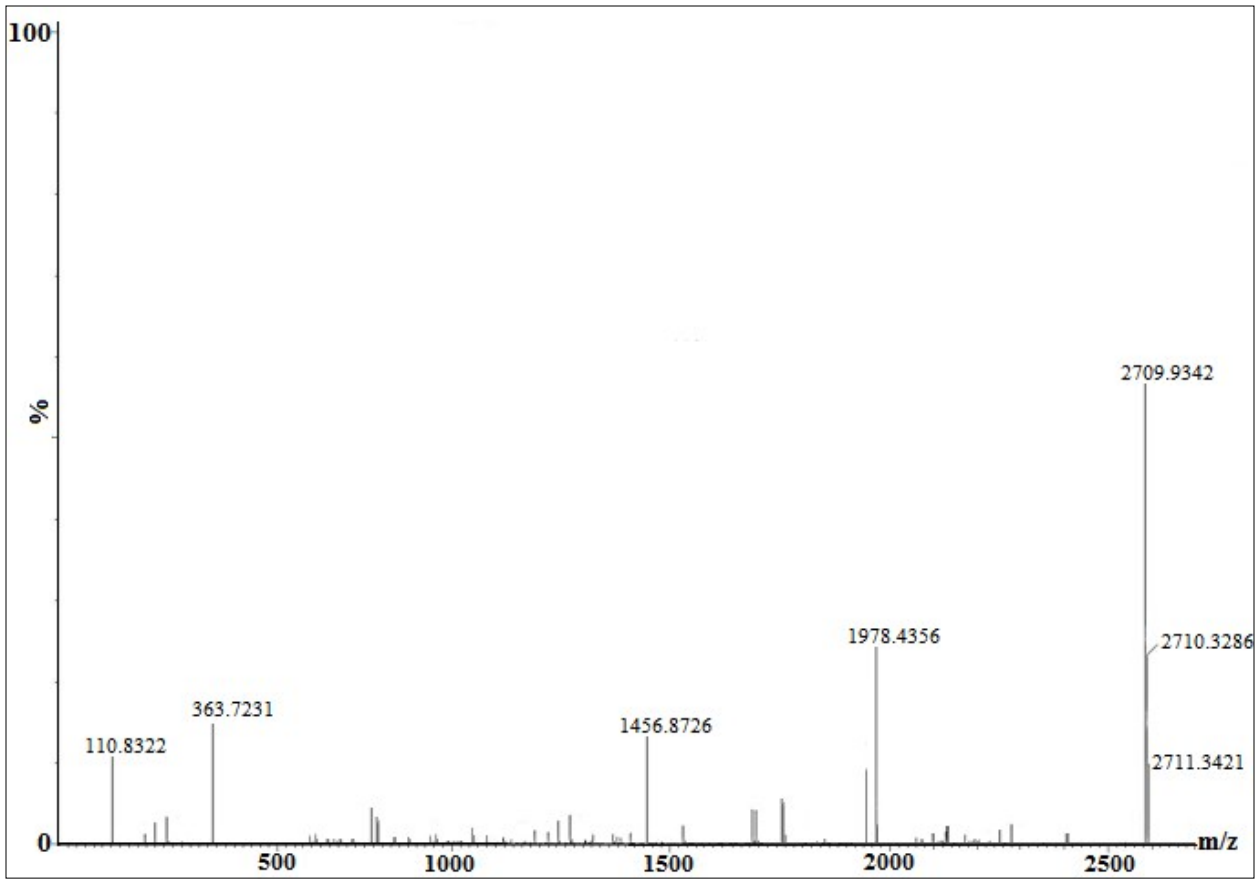

Figure S7. HRMS of compound **5b**

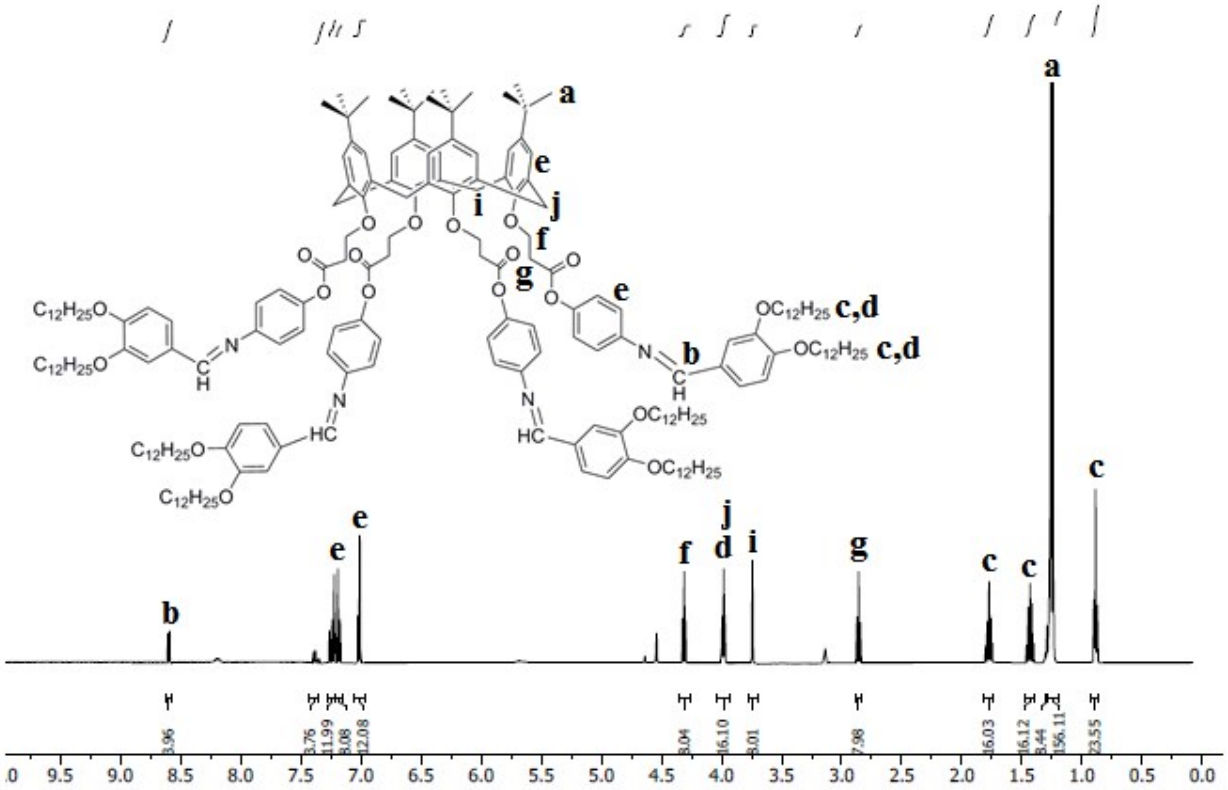

Figure S8. ^{1}H NMR of compound **5c**

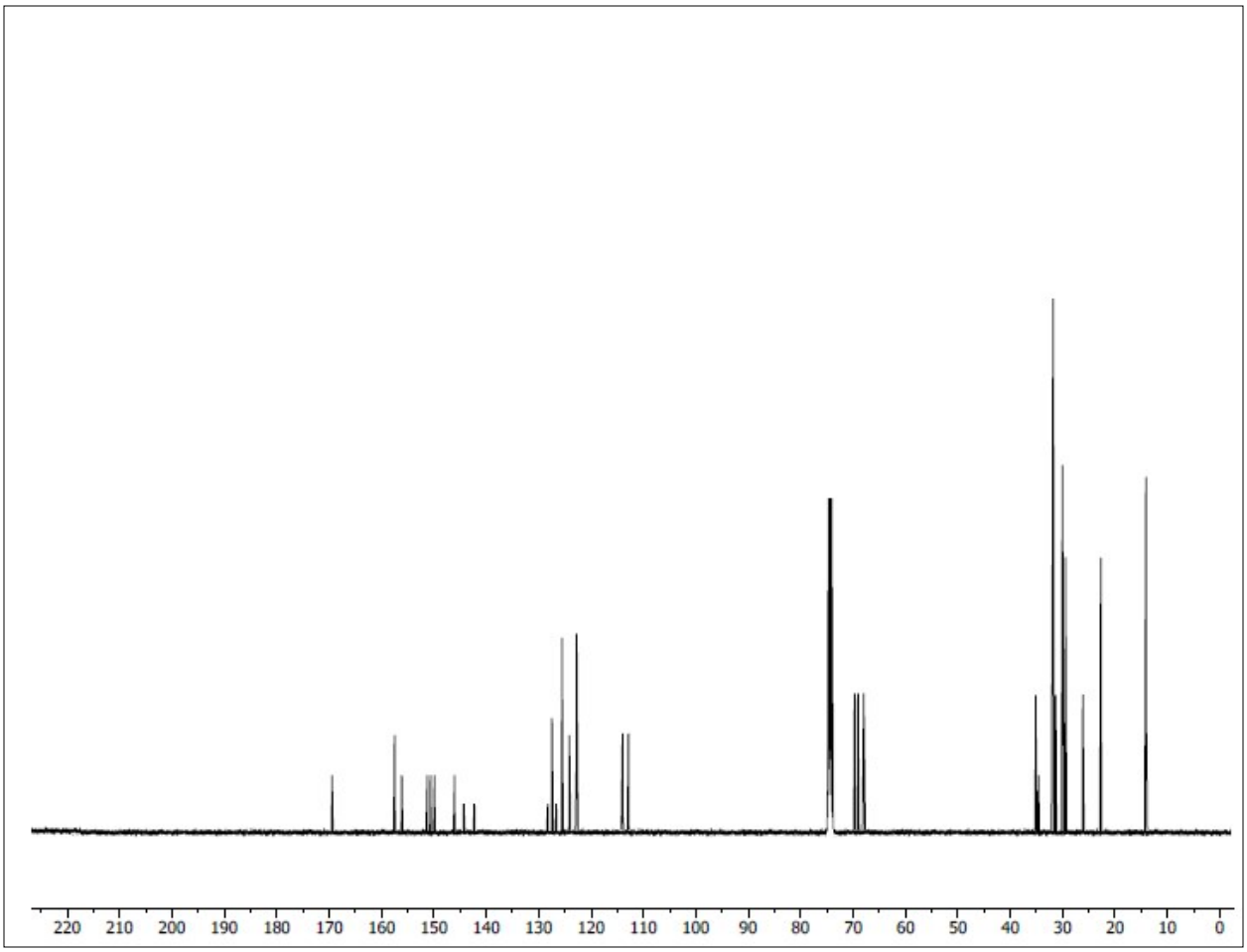

Figure S9. ^{13}C NMR of compound **5c**

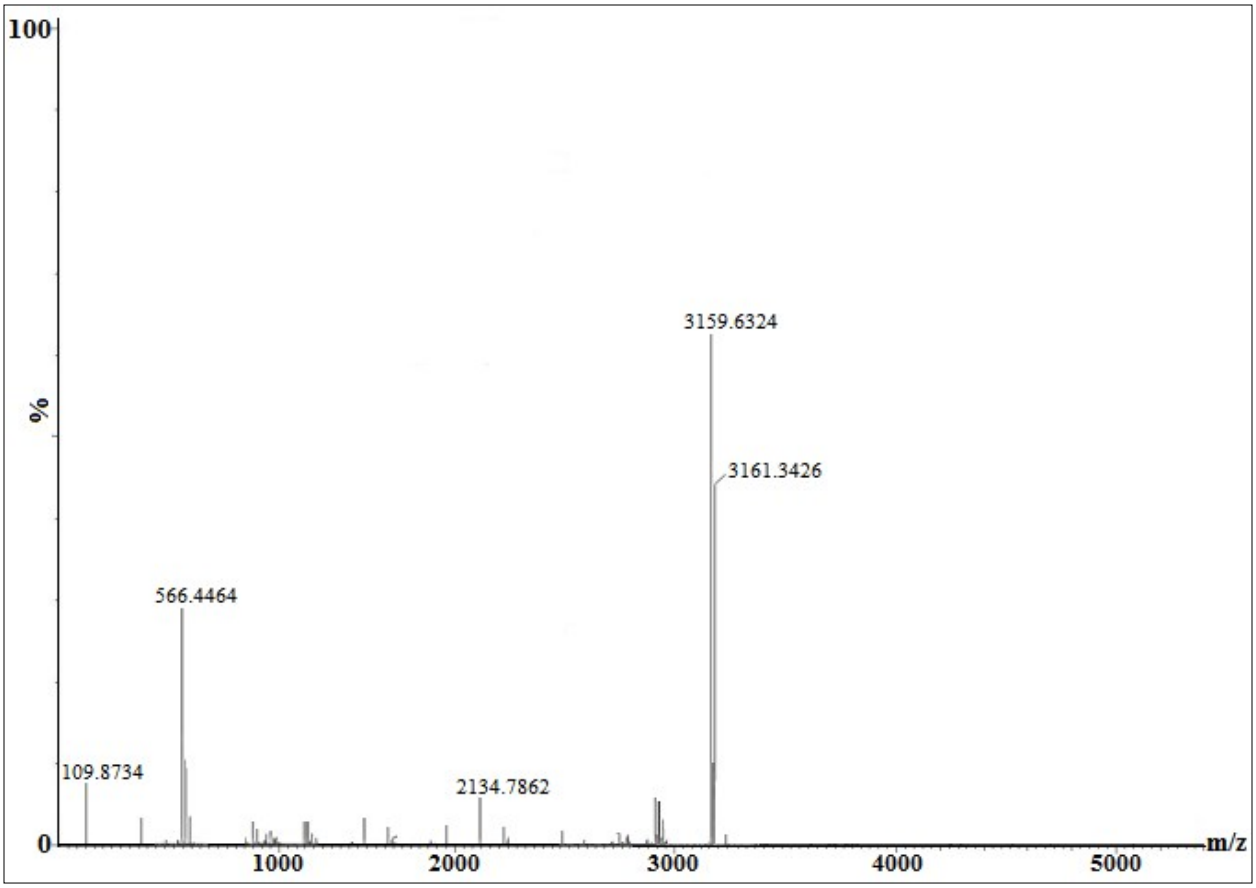

Figure S_{10}. HRMS of compound **5c**

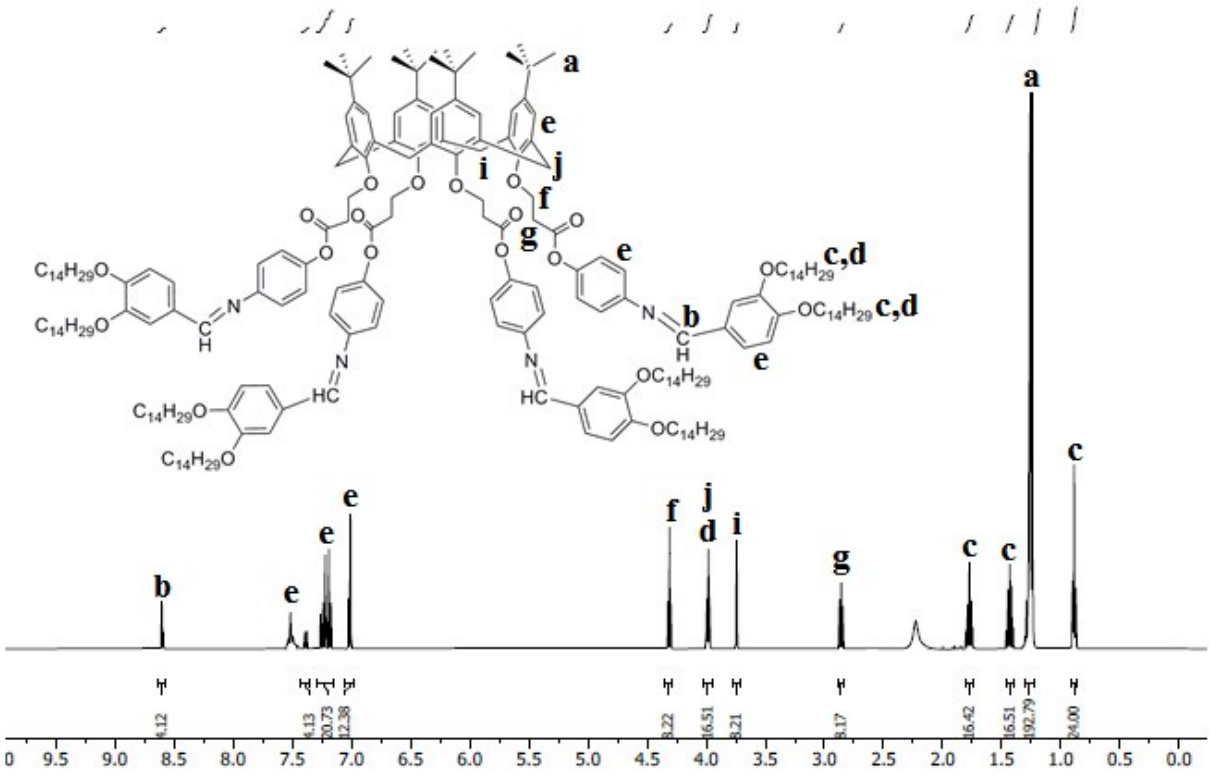

Figure S_{11}. ^{1}H NMR of compound **5d**

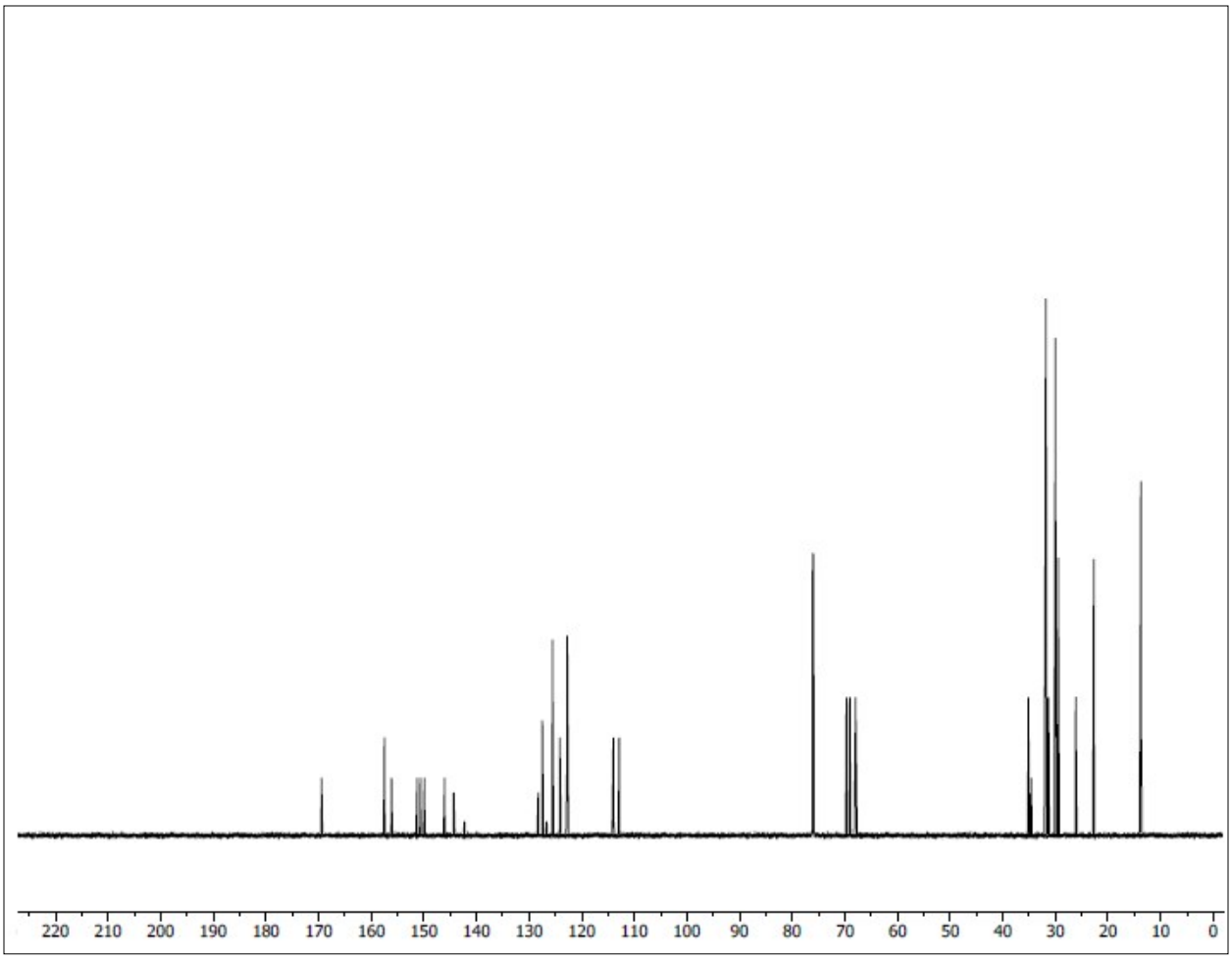

Figure S_{12}. ^{13}C NMR of compound **5d**

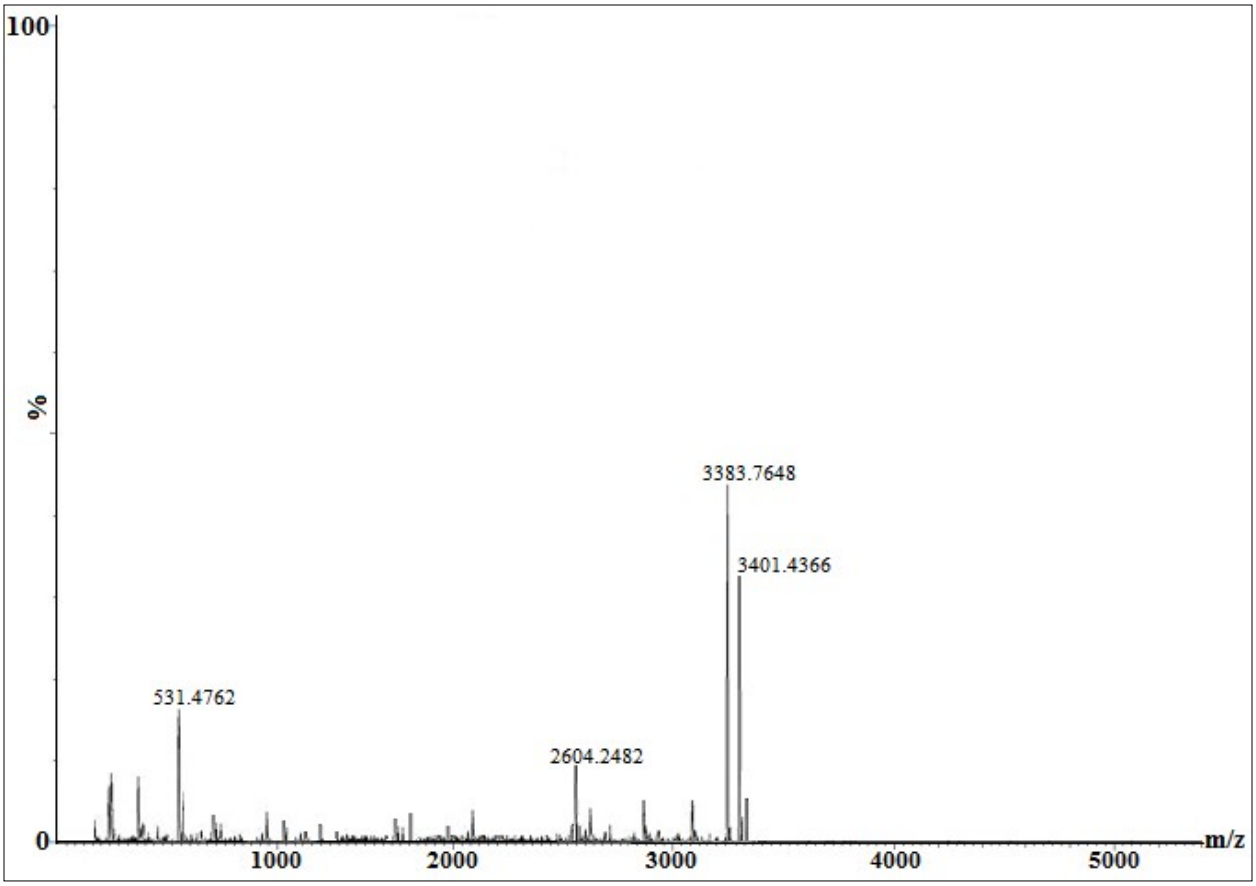

Figure S_{13}. HRMS of compound **5d**

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