Cyclotriguaiacyclene-functionalized *trans*-cinnamic acid with alkyl arms: an efficient supramolecular system for solar cell and liquid crystalline applications

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Synthesis and characterization

Melting points were taken on Opti-Melt (Automated melting point system). The FT-IR spectra were recorded on Bruker Alpha (Diamond Crystal) ATR Spectrometer in the range of 4000- 400 cm^{-1}. The texture images were studied on a trinocular optical polarizing microscope (POM) equipped with a heating stage. ^{1}H NMR spectra was recorded on a 500 MHz in Bruker Ascend 500 in the range of 0.0 ppm-16 δ ppm using $CDCl_3$ solvent and ^{13}C NMR was recorded on a 126 MHz in Bruker Ascend 500 in the range of 0.0 ppm-220 δ ppm using $CDCl_3$ and DMSO-*d6* 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.

Preparation of 4-n-alkoxy benzaldehyde (A_1-A_4)

4-n-alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1.0 mmol) with corresponding n-alkyl bromides (1.2 equiv.) in the presence of K_2CO_3 (1.2 equiv.) and dry acetone as a solvent.[1]

Preparation of *trans* 4-n-alkoxy cinnamic acid (B_1-B_4)

The resulting 4-n-alkoxybenzaldehydes **(A_1-A_4)** (1.0 mmol) were reacted with Malonic acid (1.2 mmol) in the presence of 1–2 drops piperidine as catalyst and pyridine (20 mL) as a solvent, refluxing the reaction mixture 3 to 4 hours. Afterwards, the reaction mixture is dumped in cold water. The obtained product is purified using methanol to yield corresponding *trans* 4-n-alkoxy cinnamic acids **(B_1-B_4)**.[2]

Preparation of Cyclotriveratrylene (CTV)

The cyclotriveratrylene (CTV) was synthesized using veratrole (72.4 mol), 38% aqueous formaldehyde (40 mL) and concentrated aqueous HCl (80 mL), and the resultant solution was kept stirring under a nitrogen atmosphere at 0 °C. The reaction mixture was stirred for 4 hr at ambient temperature. After the completion of the reaction, the resulting material checked by TLC (50 % ethyl acetate: hexane). Afterwards, filter the reaction mixture and wash the solid residue with ice-cold water (50 mL). Purify the residue by recrystallisation (toluene) and dry under a high vacuum to obtain Cyclotriveratrylene (CTV).[3] White precipitate, yield 76 %, IR (KBr) in cm^{-1}: 1040 (-C-H bend.), 1087 (alkoxy -OCH_3 group), 1149 (-C-H def. hydrocarbon), 1259 (-C-O-C- str.), 1344 (-C-O str.), 1463 (alkane -C-H str.), 1510 (aromatic -C=C- str.), 1606 (aromatic -C =C- str.), 2826 (-C-H str. of -CH_3), 2931 (-C-H str in -CH_3). ^{1}H NMR in δ (ppm): 3.56 (d, 6H, -CH_2-), 3.84 (s, 18H, -OCH_3), 6.83 (s, 6H, Ar-H). ^{13}C NMR: 147.73, 147.38, 131.80, 131.02, 113.69, 113.14, 56.05, 55.99, 38.27, 36.51, 34.88.

Preparation of Cyclotriguaiacyclene (CTG)

The Cyclotriguaiacyclene (CTG) was synthesized via dealkylation of CTV using $AlCl_3$ as the dealkylation reagent. CTV(1.0 mol) and $AlCl_3$ (36 equiv.) was stirred 48 hr at room temperature under nitrogen atmosphere in dichloromethane (MDC) solvent. The reaction led to demethylation of three of the six methoxy groups of CTV to yield 2,7,12-trihydroxy-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene(CTG). After the completion of the reaction, the conversion of reaction mixture was by TLC (5% methanol: MDC). Afterwards, the reaction mixture was dumped in cold water and then the product is extracted using MDC. After evaporating the MDC solvent, we get a white product. The obtained product is purified using methanol.[4] White precipitate, Yield 65 %, IR (KBr) in cm^{-1}: 1048 (-C-H bend.), 1080 (alkoxy -OCH_3 group), 1149 (-C-H def. hydrocarbon), 1250 (-C-O-C- str.), 1344 (-C-O str.), 1464 (alkane -C-H str.), 1511 (aromatic -C=C- str.), 1607 (aromatic -C =C-

str.), 2822 (-C-H str. of -CH_3), 2931 (-C-H str in -CH_3), 3195 (alcohol -O-H broad). ^{1}H NMR: 3.51 (d, 9H, -OCH_3), 3.57 (s, 6H, -CH_2-), 8.49 (s, 6H, Ar-H), 10.01 (s, 3H, -OH). ^{13}C NMR: 151.20, 151.10, 137.81, 135.67, 122.02, 119.19, 119.08, 61.20, 61.02, 45.24, 44.90, 44.74, 44.40.

Preparation of final targeted compounds ($CTGC_1$-$CTGC_4$)

The preparation of final target compounds **($CTGC_1$-$CTGC_4$)** was carried by esterification of Cyclotriguaiacyclene (1.0 mmol) and appropriate 4-n-alkoxy cinnamic acid (3.6 mmol), using EDC.HCl (3.66 mmol), and DMAP (0.6 mmol) in catalytic amount in dry CH_2Cl_2 (DCM) (30 ml) was stirred at room temperature for 48 h. After the completion of reaction, Column chromatography was used to purified the resultant crude; the desired product is eluted with dichloromethane from silica gel. Furthermore, recrystallization is carried out in chloroform to get white precipitates.[5] Yield: 62-68%. The synthetic pathway of the series is shown in Scheme-1.

Compound $CTGC_1$: IR in cm^{-1}: 829 (Poly(-CH_2-)$_n$ group in in -OCH_3 and -OC_6H_{13}), 875 (-C-H- def. di-substituted on para side -OCH_3 and -OC_6H_{13}), 957 (*trans* -CH=CH- group), 1210 (-C-O- Str.), 1252 and 1380 (str in -(CH_2-)$_n$ alkyl chain group), 1734 (-COO- ester group), 2853 and 2921 (-C-H str in -CH_3). ^{1}H NMR in δ ppm: 0.88-0.90 (t, 9H, -CH_3), 1.27-1.33 (m, 12H, CH_2), 1.42-1.48 (p, 6H, -CH_2), 1.74-1.75 (p, 6H, -CH_2), 3.79 (s, 6H, -CH_2) 3.85 (s, 9H, -OCH_3), 3.98-4.01 (t, 6H, -OCH_2), 6.26-6.29 (d, 3H, *J=15.4 Hz, trans* -CH=CH-), 6.64 (s, 3H, Ar-H), 7.02-7.04 (d, 6H, Ar-H), 7.12 (s, 3H, Ar-H), 7.71-7.74 (d, 3H, *J=15.5 Hz, trans* -CH=CH-), 7.96-7.96 (d, 6H, Ar-H). ^{13}C NMR in δ ppm: 164.25, 163.05, 158.04, 149.65, 147.64, 137.04, 131.16, 130.11, 126.20, 122.60, 121.12, 114.60, 113.12, 69.77, 68.49, 55.62, 36.62, 31.94, 29.82, 29.69, 29.59, 29.40, 29.21, 26.18, 26.07, 22.69, 14.14. MALDI Tof MS for compound **$CTGC_1$** (M+1) Calculated: 1098.5562 Found 1098.567.

Compound CTGC$_2$: IR in cm^{-1}: 837 (Poly(-CH_2-)$_n$ group in in -OCH_3 and -OC_8H_{17}), 881 (-C-H- def. di-substituted on para side -OCH_3 and -OC_8H_{17}), 961 (*trans* -CH=CH- group), 1211 (-C-O- Str.), 1244 and 1381 (str in -(CH_2-)$_n$ alkyl chain group), 1731 (-COO- ester group), 2854 and 291 (-C-H str in -CH_3). ^{1}H NMR in δ ppm: 0.89-0.90 (t, 9H, -CH_3), 1.26-1.33 (m, 12H, CH_2), 1.42-1.48 (p, 6H, -CH_2), 1.74-1.79 (p, 6H, -CH_2), 3.75 (s, 6H, -CH_2) 3.84 (s, 9H, -OCH_3), 4.00-4.01 (t, 6H, -OCH_2), 6.31-6.34 (d, 3H, *J=15.1 Hz*, *trans* -CH=CH-), 6.67 (s, 3H, Ar-H), 7.02-7.04 (d, 6H, Ar-H), 7.12 (s, 3H, Ar-H), 7.82-7.85 (d, 3H, *J=15.1 Hz*, *trans* -CH=CH-), 7.99-7.99 (d, 6H, Ar-H). ^{13}C NMR in δ ppm: 164.34, 163.08, 158.15, 149.67, 147.69, 137.08, 131.13, 130.16, 126.23, 122.66, 121.14, 114.77, 113.13, 69.74, 68.18, 55.59, 36.64, 31.95, 31.05, 29.71, 29.61, 29.40, 29.21, 26.07, 22.71, 14.14. MALDI Tof MS for compound **CTGC$_2$** (M+1) Calculated: 1182.6456 Found 1082.653.

Compound CTGC$_3$: IR in cm^{-1}: 831 (Poly(-CH_2-)$_n$ group in in -OCH_3 and -$OC_{10}H_{21}$), 871 (-C-H- def. di-substituted on para side -OCH_3 and -$OC_{10}H_{21}$), 966 (*trans* -CH=CH- group), 1203 (-C-O- Str.), 1249 and 1377 (str in -(CH_2-)$_n$ alkyl chain group), 1731 (-COO- ester group), 2853 and 2915 (-C-H str in -CH_3). ^{1}H NMR in δ ppm: 0.89-0.90 (t, 9H, -CH_3), 1.25-1.34 (m, 12H, CH_2), 1.47-1.51 (p, 6H, -CH_2), 1.81-1.82 (p, 6H, -CH_2), 3.78 (s, 6H, -CH_2) 3.84 (s, 9H, -OCH_3), 4.00-4.01 (t, 6H, -OCH_2), 6.31-6.34 (d, 3H, *J=15.5 Hz*, *trans* -CH=CH-), 6.67 (s, 3H, Ar-H), 7.02-7.04 (d, 6H, Ar-H), 7.12 (s, 3H, Ar-H), 7.82-7.85 (d, 3H, *J=15.2 Hz*, trans -CH=CH-), 7.99-7.99 (d, 6H, Ar-H). ^{13}C NMR in δ ppm: 164.37, 163.01, 158.65, 149.62, 147.69, 137.04, 131.40, 130.13, 126.26, 122.62, 121.12, 114.72, 113.11, 69.59, 68.10, 55.07, 36.63, 31.94, 29.89, 29.71, 29.69, 29.62, 29.32, 29.26, 26.18, 26.03, 22.71, 14.12. MALDI Tof MS for compound **CTGC$_3$** (M+1) Calculated: 1266.7463 Found 1266.755.

Compound CTGC$_4$: IR in cm^{-1}: 823 (Poly(-CH_2-)$_n$ group in in -OCH_3 and -$OC_{14}H_{29}$), 871 (-C-H- def. di-substituted on para side -OCH_3 and -$OC_{14}H_{29}$), 949 (*trans* -CH=CH- group), 1208 (-C-O- Str.), 1251 and 1369 (str in -(CH_2-)$_n$ alkyl chain group), 1729 (-COO- ester group), 2859 and 2922 (-C-H str in -CH_3). ^{1}H NMR in δ ppm: 0.89-0.90 (t, 9H, -CH_3), 1.26-1.34 (m, 12H, -CH_2), 1.47-1.51 (p, 6H, -CH_2), 1.84-1.85 (p, 6H, -CH_2), 3.78 (s, 6H, -CH_2) 3.84 (s, 9H, -OCH_3), 3.99-4.01 (t, 6H, -OCH_2), 6.26-6.29 (d, 3H, *J = 15.2 Hz*, *trans* -CH=CH-), 6.64 (s, 3H, Ar-H), 7.02-7.04 (d, 6H, Ar-H), 7.12 (s, 3H, Ar-H), 7.71-7.74 (d, 3H, *J=15.2 Hz*, *trans* -CH=CH-), 7.96-7.96 (d, 6H, Ar-H). ^{13}C NMR in δ ppm: 164.26, 163.05, 158.25, 149.22, 147.99, 137.00, 131.94, 130.22, 126.22, 122.89, 121.22, 114.77, 113.55, 69.56, 68.15, 55.71, 36.69, 31.90, 29.86, 29.62, 29.40, 26.18, 26.08, 22.71, 14.14. MALDI Tof MS for compound **CTGC$_4$** (M+1) Calculated: 1434.9235 Found 1434.934.

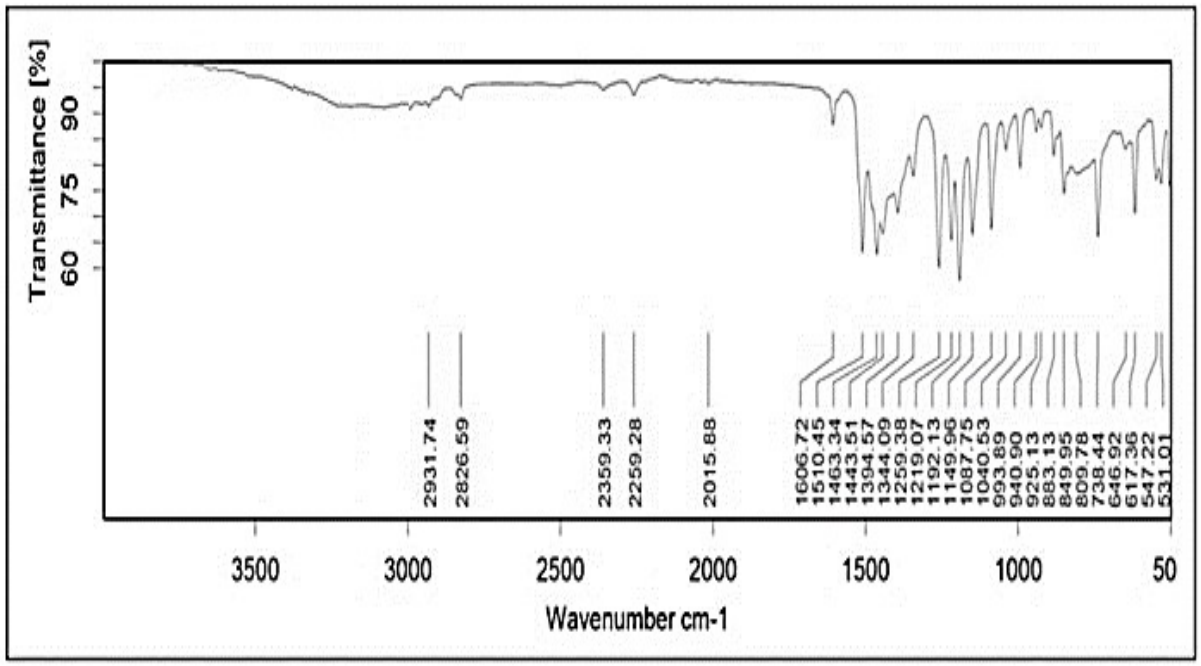

Figure S_1. The IR spectrum of CTV.

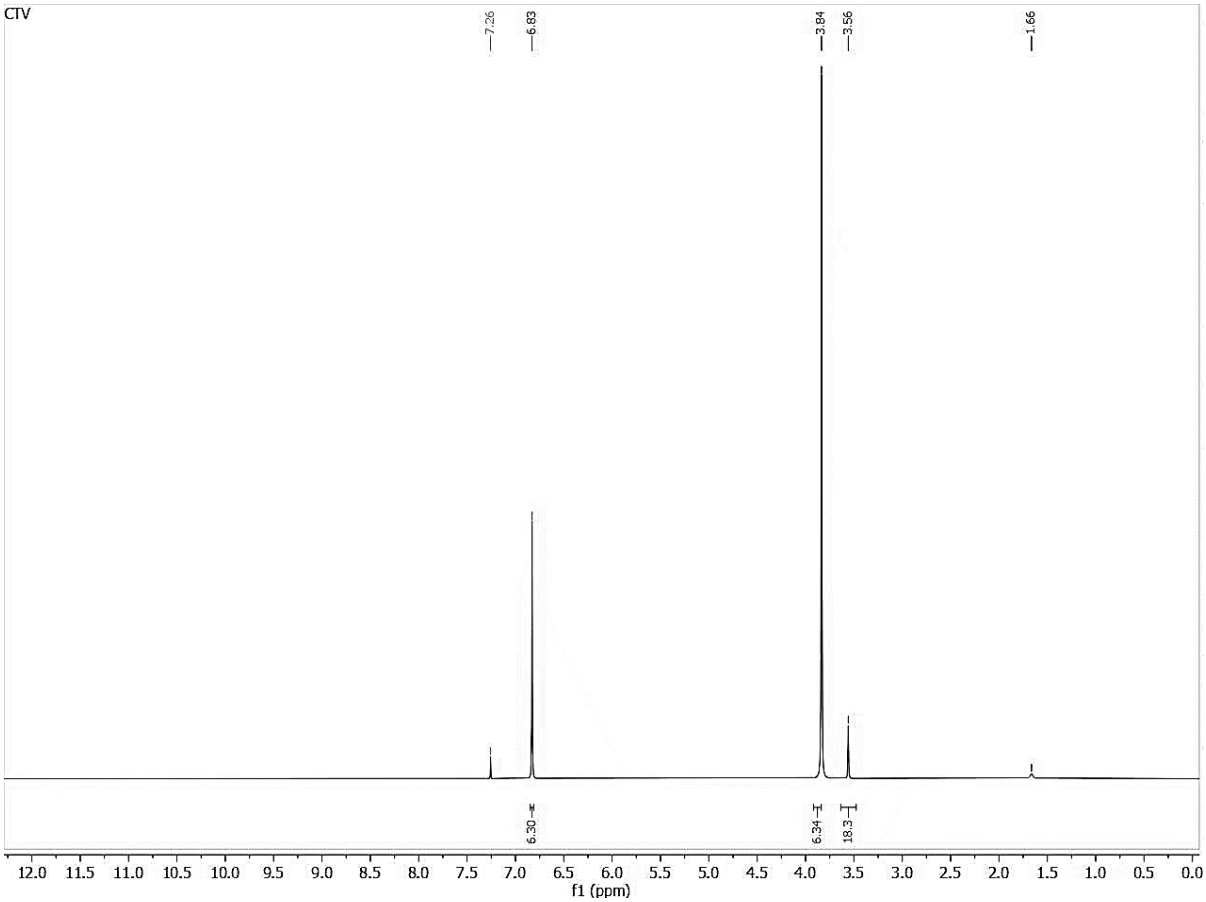

Figure S_2. The ^{1}H NMR spectrum of CTV.

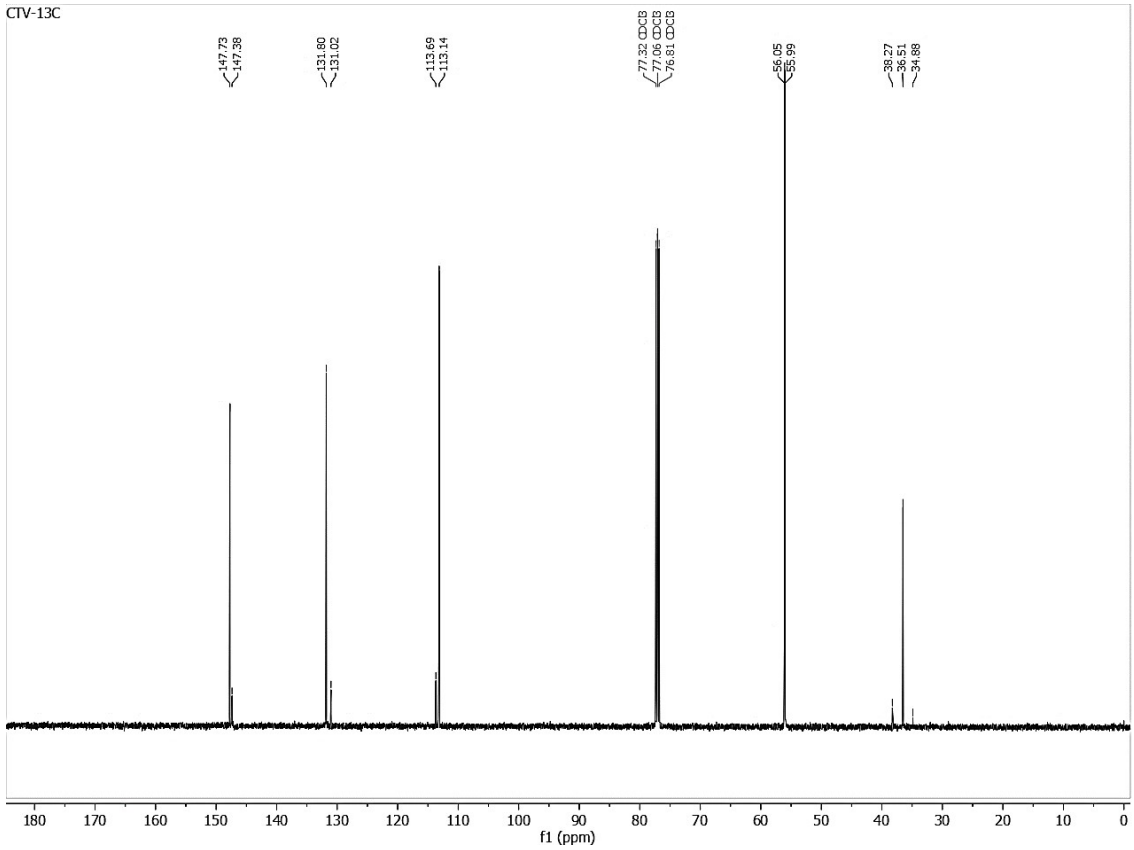

Figure S_3. The ^{13}C NMR spectrum of CTV.

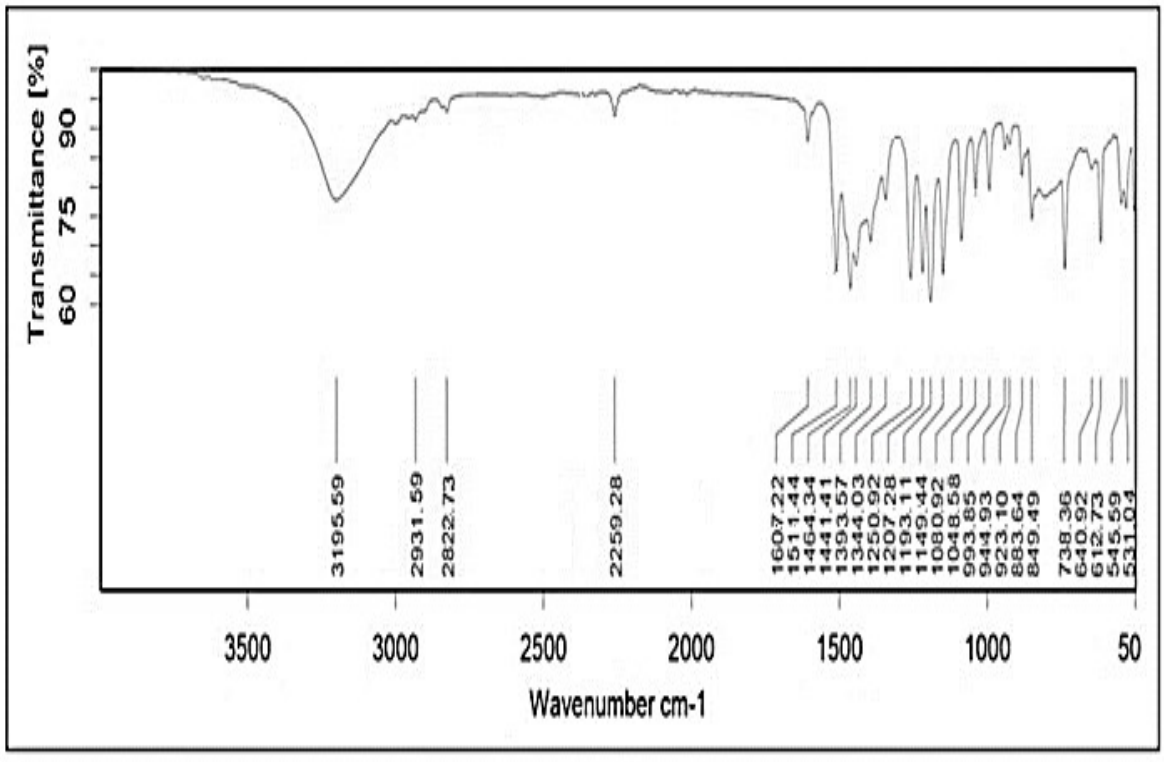

Figure S_4. The IR spectrum of CTG.

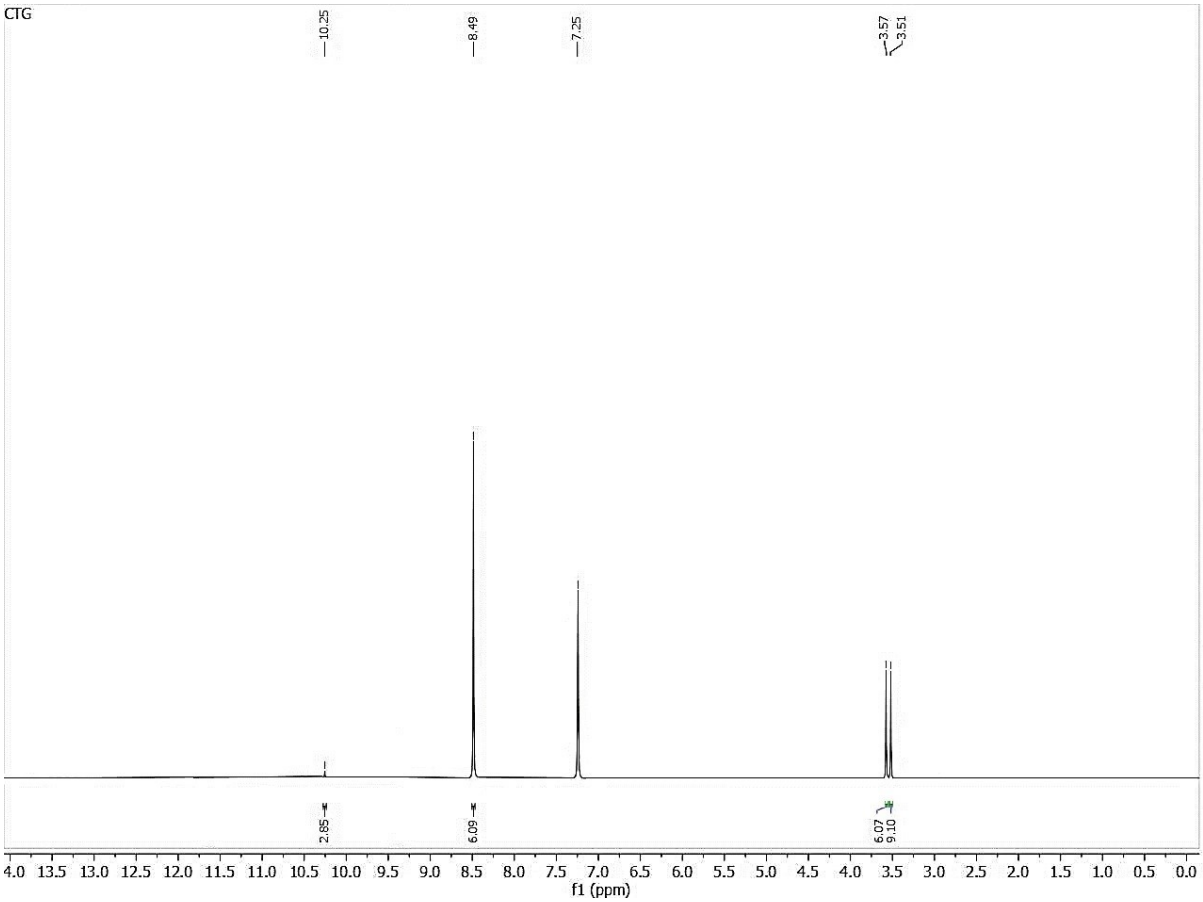

Figure S_5. The ^{1}H NMR spectrum of CTG.

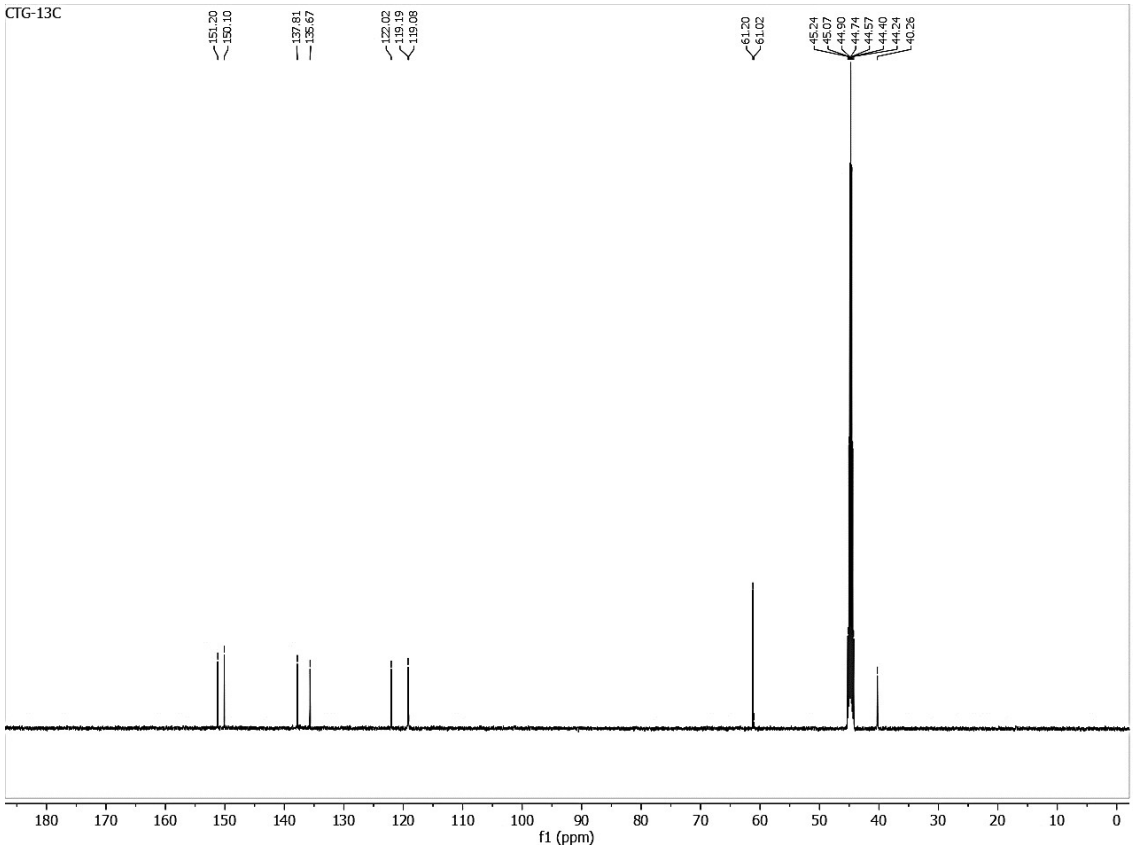

Figure S_6. The ^{13}C NMR spectrum of CTG.

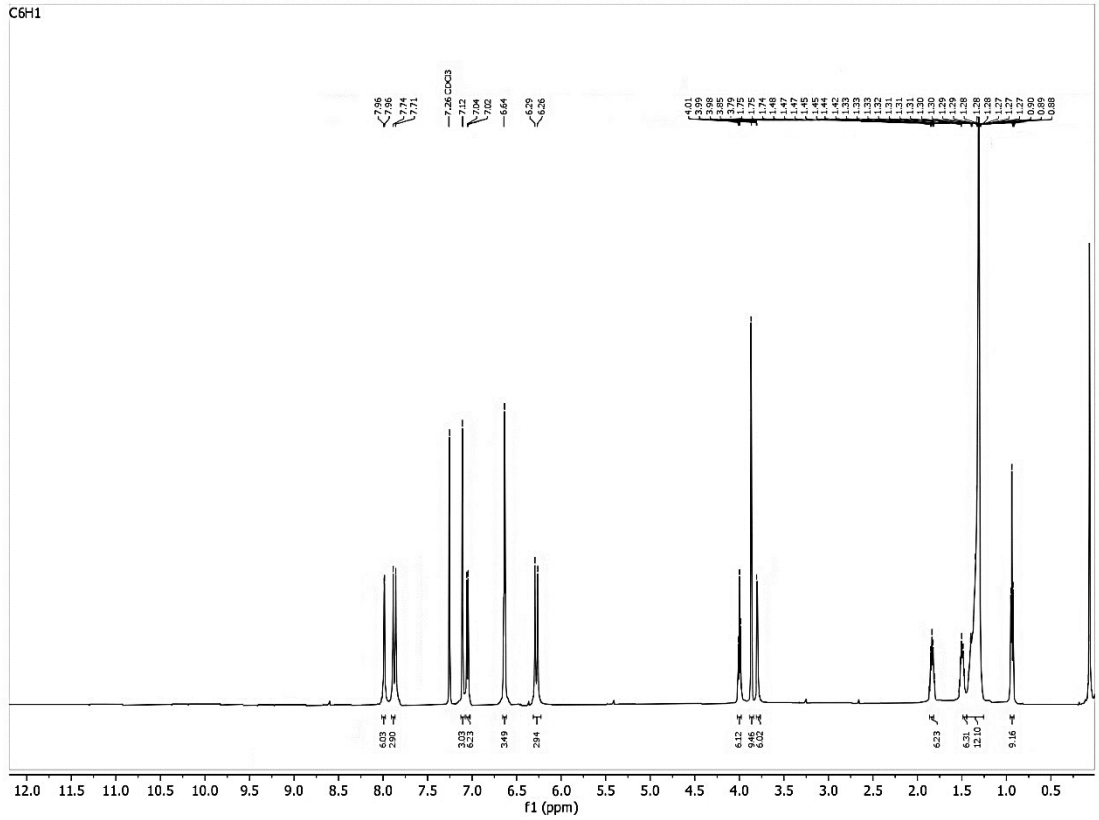

Figure S_7. ^{1}H-NMR spectra of compound **$CTGC_1$**.

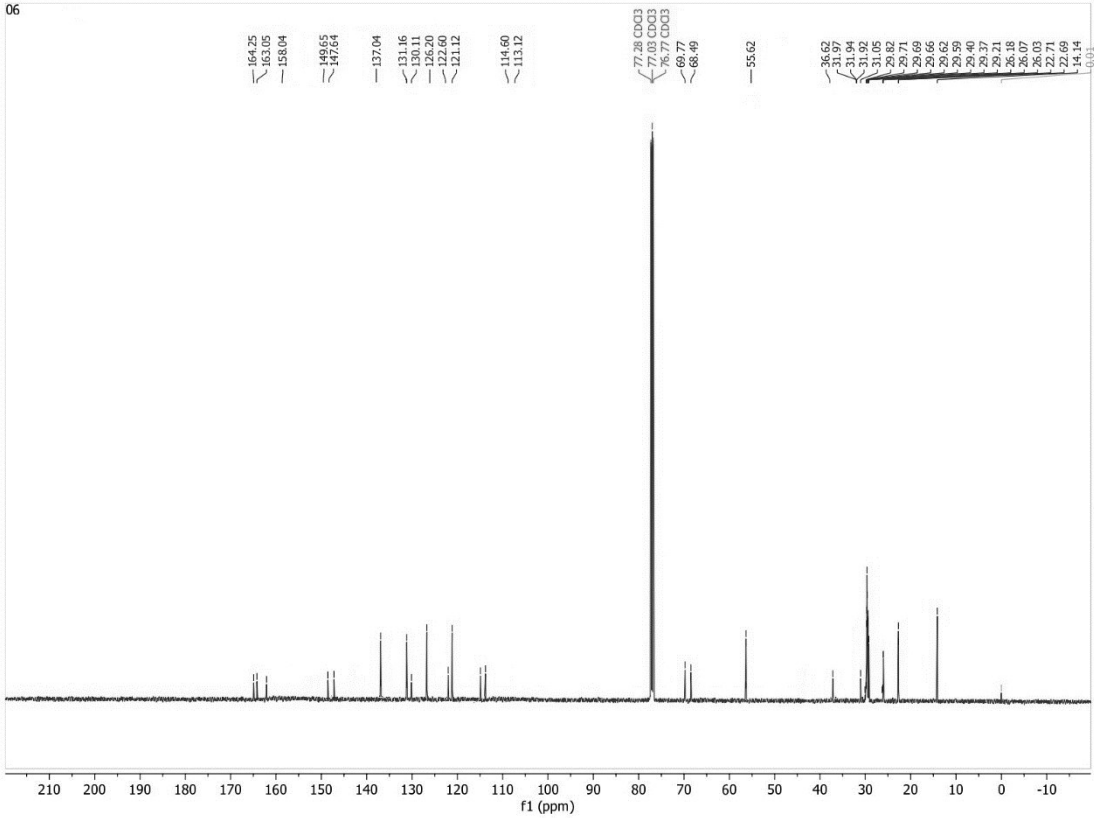

Figure S_8. ^{13}C-NMR spectra of compound **$CTGC_1$**.

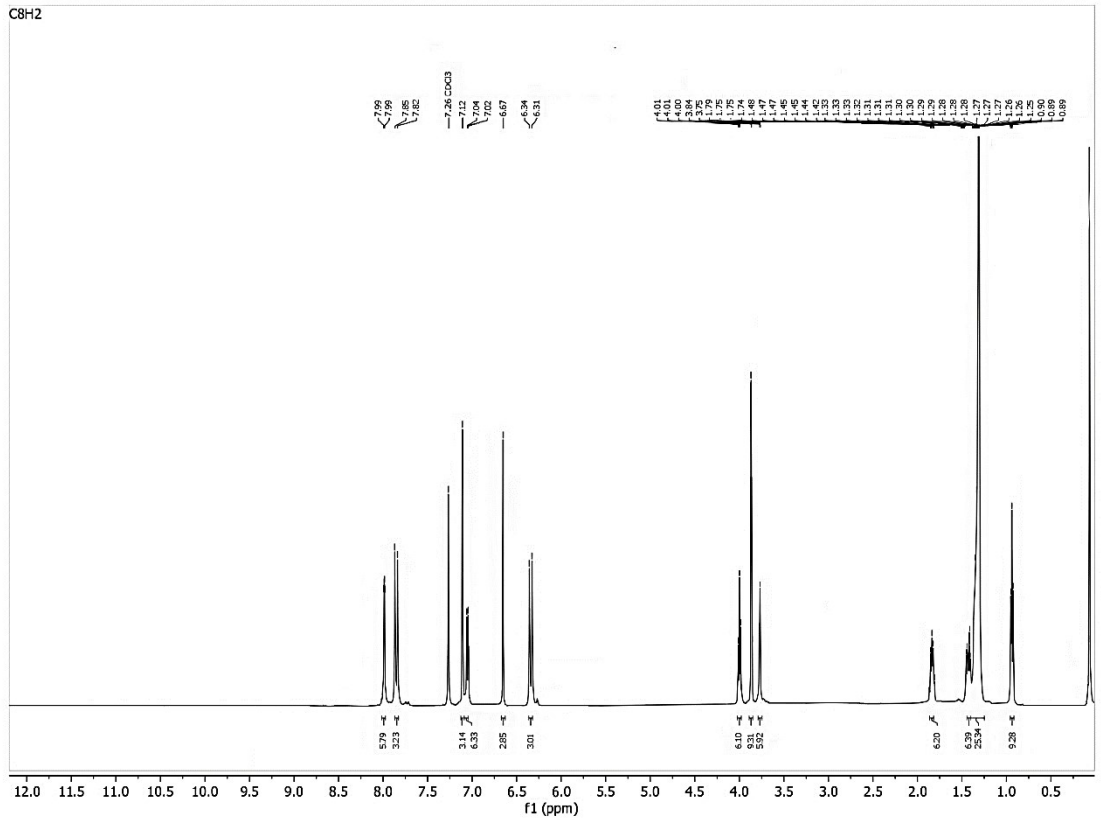

Figure S_9. ^{1}H-NMR spectra of compound **$CTGC_2$**.

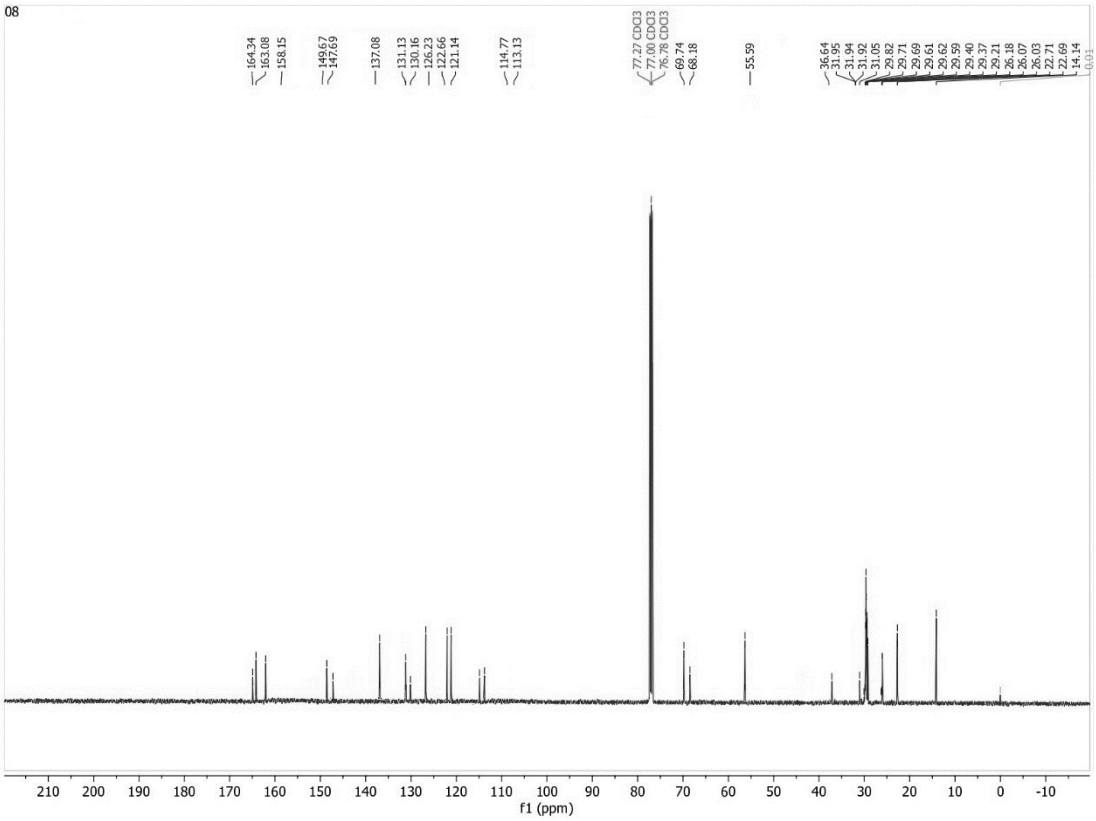

Figure S_{10}. ^{13}C-NMR spectra of compound **$CTGC_2$**.

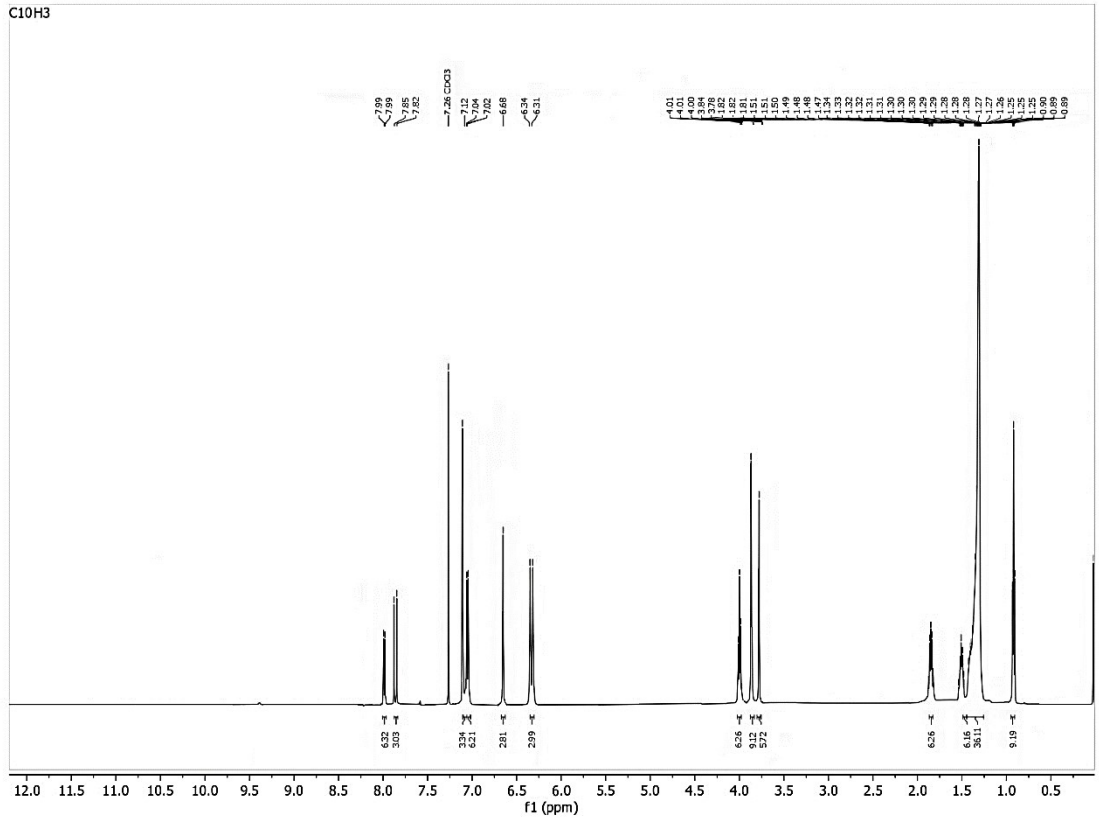

Figure S_{11}. ^{1}H-NMR spectra of compound **$CTGC_3$**.

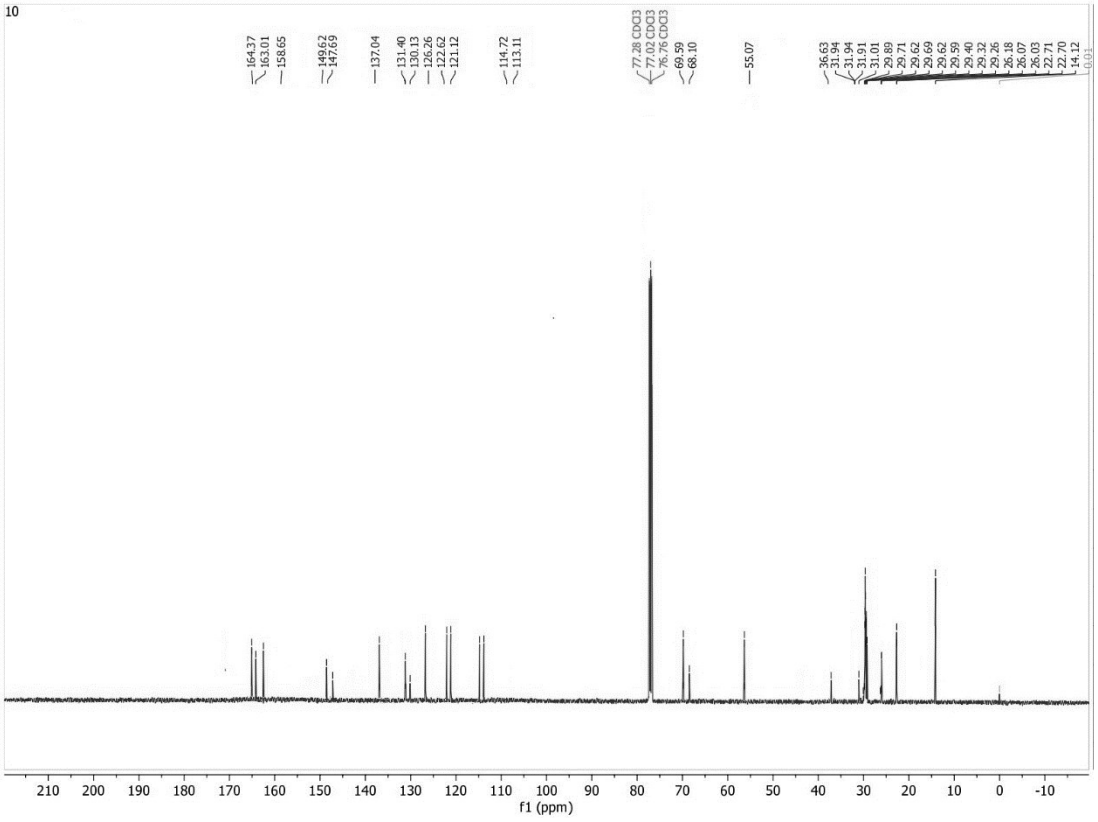

Figure S_{12}. ^{13}C-NMR spectra of compound **$CTGC_3$**.

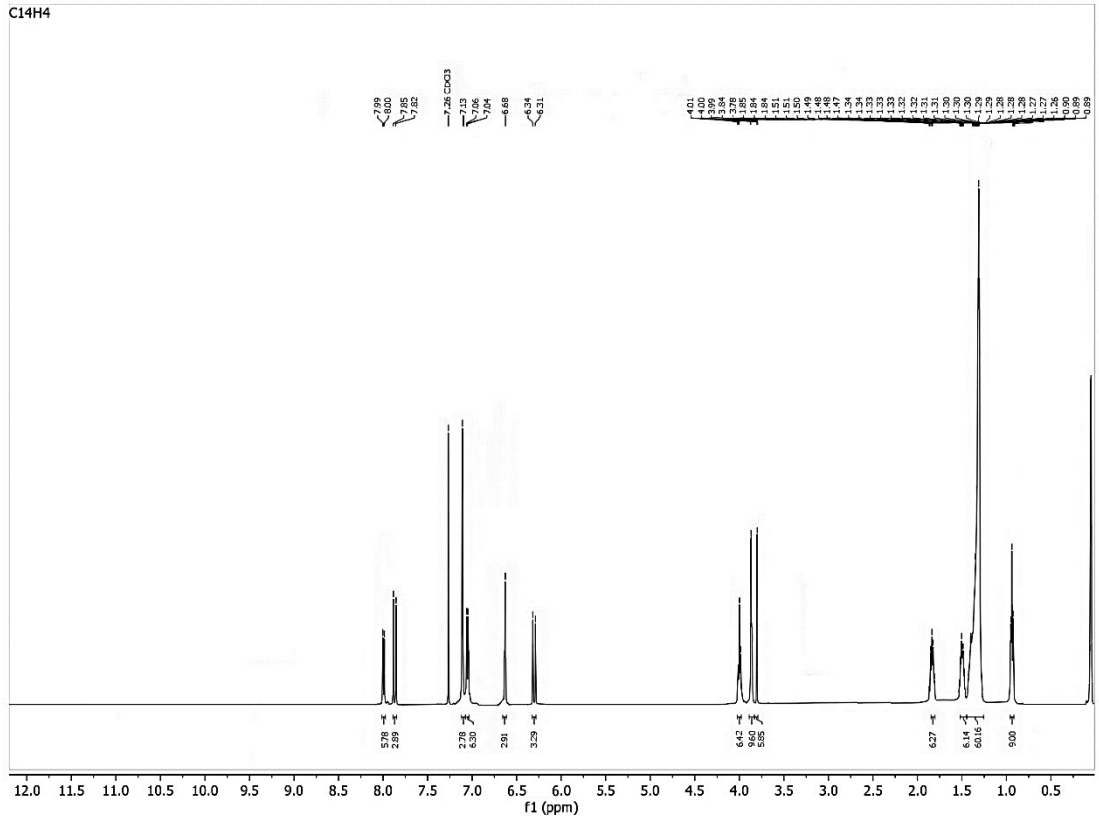

Figure S_{13}. ^{1}H-NMR spectra of compound **$CTGC_4$**.

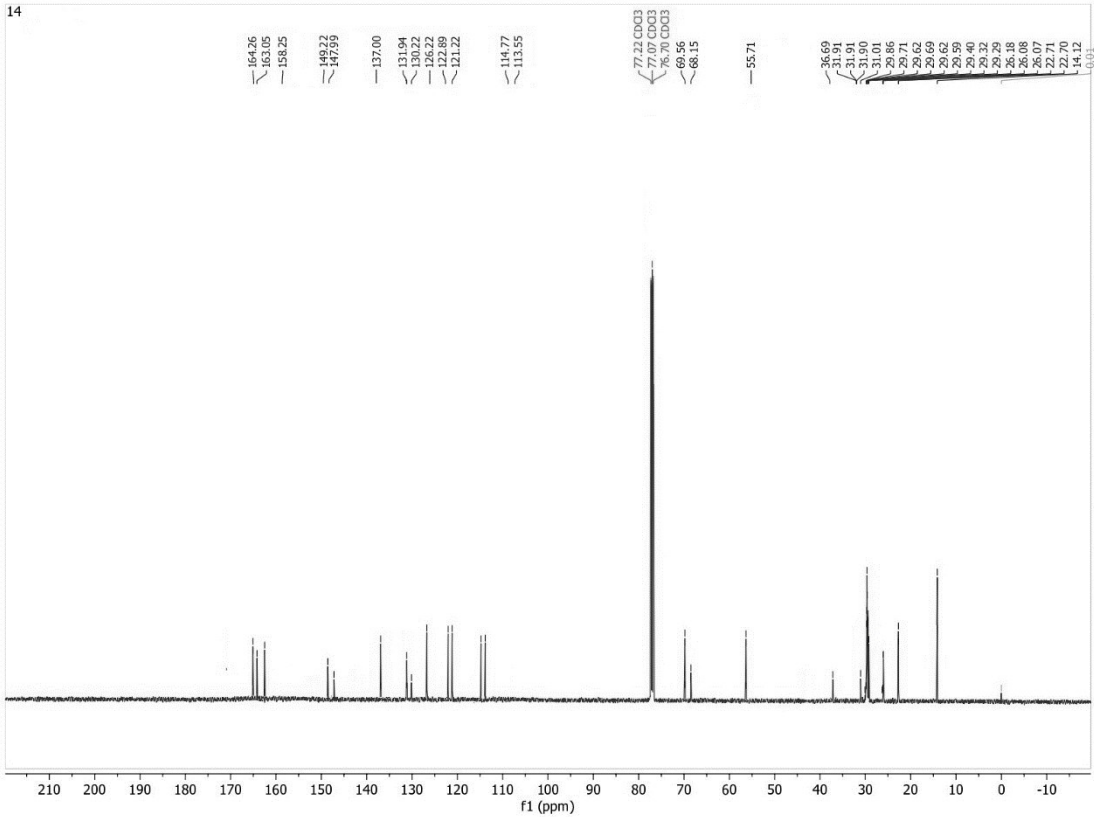

Figure S_{14}. ^{13}C-NMR spectra of compound **$CTGC_4$**.

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