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Resorcinarene appended octa-substituted alkyl arms: a new strategy to fabricate supramolecular material for liquid crystal and solar-cell application

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Synthesis and Characterization

Thin layer chromatography (TLC) was carried out using silica gel Si 60-F254 (Merck) for reaction monitoring using Dichloromethane: Methanol (9.5:0.5 V/V) as mobile phase and observed under ultraviolet (UV) light. Purifications were carried out by using commercial-grade solvents. Melting points were taken on Opti-Melt (automated melting point apparatus). 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 Nikon Eclipse LV-100 POL optical polarizing microscope (POM) equipped with a LTSE 420 heating plate (Linkam Scientific Instruments, Tadworth, Surrey, UK) and texture were captured by attached digital camera. The mesophase type was identified by visual comparison with known phase standards. The ^{1}H-NMR spectra were recorded on Bruker (Ascend 500) 500MHz spectrometer using Deuterochloroform ($CDCl_3$) as a solvent, TMS as the internal reference. In ^{1}H-NMR, chemical shifts were reported in δ (ppm), and signals were reported as singlet (s), doublet (d), triplet (t), multiplate (m). ^{13}C NMR spectra were recorded on Bruker Ascend 500 126MHz spectrometer using Deuterochloroform ($CDCl_3$) as a solvent, TMS as the internal reference. In ^{1}H-NMR, chemical shifts were reported in δ (ppm).

Preparation of compound (C)

Compound **C** was synthesized by refluxing 1,3-dimethoxy benzene and 3,4-hydroxybenzaldehyde using acid catalyst. 1,3-dimethoxy benzene (3.82 mmol) was stirred in ethanol, then conc. HCl (9.0M, 0.8 mL) was added drop-wise at room temperature.[1] Then drop-wise, 3,4-dihydroxybenzaldehyde (3.82 mmol) was added to reaction mixture. The reaction mixture was then stirred for 72 h. at refluxing temperature. The reaction was monitored by TLC after that the reaction mixture was cooled to room temperature and put into ice-water. The obtained product were washed with cold methanol and dry in a 50 ^{0}C oven afforded light pink solid of Octa-O-methoxy resorcin[4]arene (compound **C**). Yield: 73%, M.P.: 390 ^{0}C, FT-IR (Dimond crystal) in cm^{-1}; 3462.47 (-OH, phenols), 2930.75 (-C-H, alkane, stretching), 1583, 1505 (-C=C-, Aromatic), 1457 (-C-H, Alkane, bending), 1197, 1022 (-C-O-, ethers), 810 (=C-H, meta-aromatic bending), 621 (-C-C-, alkane). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.89 (s, 8H, -OH), 7.20 (s, 4H, ArH), 7.10 (d, 4H, ArH, J =7.9 Hz), 7.6 (d, 4H, ArH, J =7.7 Hz), 6.93 (s, 4H, ArH), 6.88 (s, 4H, ArH), 5.28 (s, 4H, -CH), 3.83 (s, 24H, -OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 157.77, 147.04, 145.14, 138.61, 132.02, 122.10, 121.71, 115.00, 114.37, 98.02, 55.51, 31.91. MALDI Tof MS for compound **C** (M+1) Calculated: 1033.0932 Found 1034.134.

Preparation of 2,4,6,8-tetrakis(3,4-dibutoxyphenyl)-1^4,1^6,3^4,3^6,5^4,5^6,7^4,7^6-octamethoxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (D_1)

Compound **C** (1.031 mmol) and anhydrous K_2CO_3 were dissolved in DMF, then the reaction mixture was stirred for 30 minutes at room temperature. Then butyl bromide (8.8 mole equivalent) were added drop-wise in the mixture and heated in an oil bath at reflux temperature for 24 h. TLC was used to monitor the reaction using dichloromethane: methanol (9.5:0.5 V/V)

mobile phase, to ensure that whole starting ingredients has been consumed.[2] The RBF then cooled to room temperature, and then quenched in ice-water. The resultant crude residue was refined by using methanol trituration to obtain light brown solid compound **D_1**, Yield: 69%, FT-IR (Diamond crystal) in cm^{-1}: 2913 (-C-H alkane, stretching), 2874 (-C-H alkane, stretching(methoxy), 1578, 1495 (-C=C- Aromatic), 1447, 1399 (-C-H Alkane, bending), 1153, 1051, 1036 (-C-O- ethers), 823 (=C-H Aromatic bending). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.11 (s, 4H, ArH), 6.94 (d, 4H, ArH, *J* =7.8 Hz), 6.90 (d, 4H, ArH, *J*= 7.4 Hz), 6.81 (s, 4H, ArH), 6.62 (s, 4H, ArH) 5.33 (s, 4H, -CH), 4.10 (t, 16H, -OCH_2-) 3.76 (s, 24H, -OCH_3), 1.81 (m, 16H, -CH_2) 1.46 (m, 16H, -CH_2), 0.88 (t, 24H, -CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 157.11, 149.59, 149.23, 135.33, 130.59, 121.59, 119.59, 114.15, 113.29, 99.82, 68.29, 58.05, 34.10, 31.93, 29.67, 29.64, 29.60, 29.56, 26.36, 29.11, 26.34, 25.98, 22.70, 14.13. MALDI Tof MS for compound **D_1** (M+1) Calculated: 1481.9623 Found 1482.842.

Preparation of 2,4,6,8-tetrakis(3,4-bis(hexyloxy)phenyl)-1^4,1^6,3^4,3^6,5^4,5^6,7^4,7^6-octamethoxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (D_2)

Brown solid, Yield: 66 %, FT-IR (Diamond crystal) in cm^{-1}: 2912 (-C-H alkane, stretching), 2871 (-C-H alkane, stretching (methoxy), 1580, 1492 (-C=C- Aromatic), 1446, 1397 (-C-H Alkane, bending), 1158, 1049, 1028 (-C-O- ethers), 822 (=C-H Aromatic bending). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.10 (s, 4H, ArH), 6.96 (d, 4H, ArH, *J* =7.7 Hz), 6.91 (d, 4H, ArH, *J* =7.4 Hz), 6.80 (s, 4H, ArH), 6.62 (s, 4H, ArH) 5.31 (s, 4H, -CH), 4.09 (t, 16H, -OCH_2-) 3.75 (s, 24H, -OCH_3), 1.76 (m, 16H, -CH_2) 1.56 (m, 16H, -CH_2), 1.31 (m, 32H, -CH_2), 0.88 (t, 24H, -CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 156.88, 150.91, 149.78, 136.43, 130.59, 121.31, 119.29, 114.14, 113.35, 99.38, 68.29, 58.48, 14.13. MALDI Tof MS for compound **D_2** (M+1) Calculated: 1706.3943 Found 1707.464.

Preparation of 2,4,6,8-tetrakis(3,4-bis(octyloxy)phenyl)-1^4,1^6,3^4,3^6,5^4,5^6,7^4,7^6-octamethoxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (D_3)

Light yellow solid, Yield: 73 % FT-IR (Diamond crystal) in cm^{-1}: 2914 (-C-H alkane, stretching), 2848 (-C-H alkane, stretching(methoxy), 1576, 1501 (-C=C- Aromatic), 145, 1376 (-C-H Alkane, bending), 115, 1095, 1026 (-C-O- ethers), 826 (=C-H Aromatic bending). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.10 (s, 4H, ArH), 6.94 (d, 4H, ArH, J =7.8 Hz), 6.90 (d, 4H, ArH, J =7.3 Hz), 6.80 (s, 4H, ArH), 6.62 (s, 4H, ArH) 5.29 (s, 4H, -CH), 4.09 (t, 16H, -OCH_2-) 3.75 (s, 24H, -OCH_3), 1.80 (m, 16H, -CH_2) 1.46 (m, 16H, -CH_2), 1.33 (m, 64H, -CH_2), 0.88 (t, 24H, -CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 157.18, 149.56, 148.20, 135.67, 130.59, 121.81, 120.13, 114.14, 112.73, 96.66, 68.28, 56.36, 34.78, 31.94, 29.71, 29.69, 29.67, 29.60, 29.56, 29.37. 29.11, 26.33, 25.99, 22.70, 14.13. MALDI Tof MS for compound **D_3** (M+1) Calculated: 1930.8232 Found 1931.943.

Preparation of 2,4,6,8-tetrakis(3,4-bis(decyloxy)phenyl)-1^4,1^6,3^4,3^6,5^4,5^6,7^4,7^6-octamethoxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (D_4)

Light brown solid, Yield: 78 % FT-IR (Diamond crystal) in cm^{-1}: 291 (-C-H alkane, stretching), 28506 (-C-H alkane, stretching (methoxy), 157, 1501 (-C=C- Aromatic), 1443, 138 (-C-H Alkane, bending), 1184, 1087, 102 (-C-O- ethers), 826 (C-H Aromatic bending). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.10 (s, 4H, ArH), 6.95 (d, 4H, ArH, J =7.7 Hz), 6.89 (d, 4H, ArH, J =7.6 Hz), 6.80 (s, 4H, ArH), 6.62 (s, 4H, ArH) 5.30 (s, 4H, -CH), 4.09 (t, 16H, -OCH_2-) 3.7 (s, 24H, -OCH_3), 1.82 (m, 16H, -CH_2) 1.46 (m, 16H, -CH_2), 1.34 (m, 96H, -CH_2), 0.88 (t, 24H, -CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 156.29, 149.25, 148.70, 134.84, 130.46, 121.18, 119.82, 114.92, 113.84, 99.68, 68.23, 56.36, 35.39, 31.76, 30.48, 29.89, 29.47, 29.16, 28.88, 25.02, 22.56, 14.43. MALDI Tof MS for compound **D_4** (M+1) Calculated: 2155.2564 Found 2156.364.

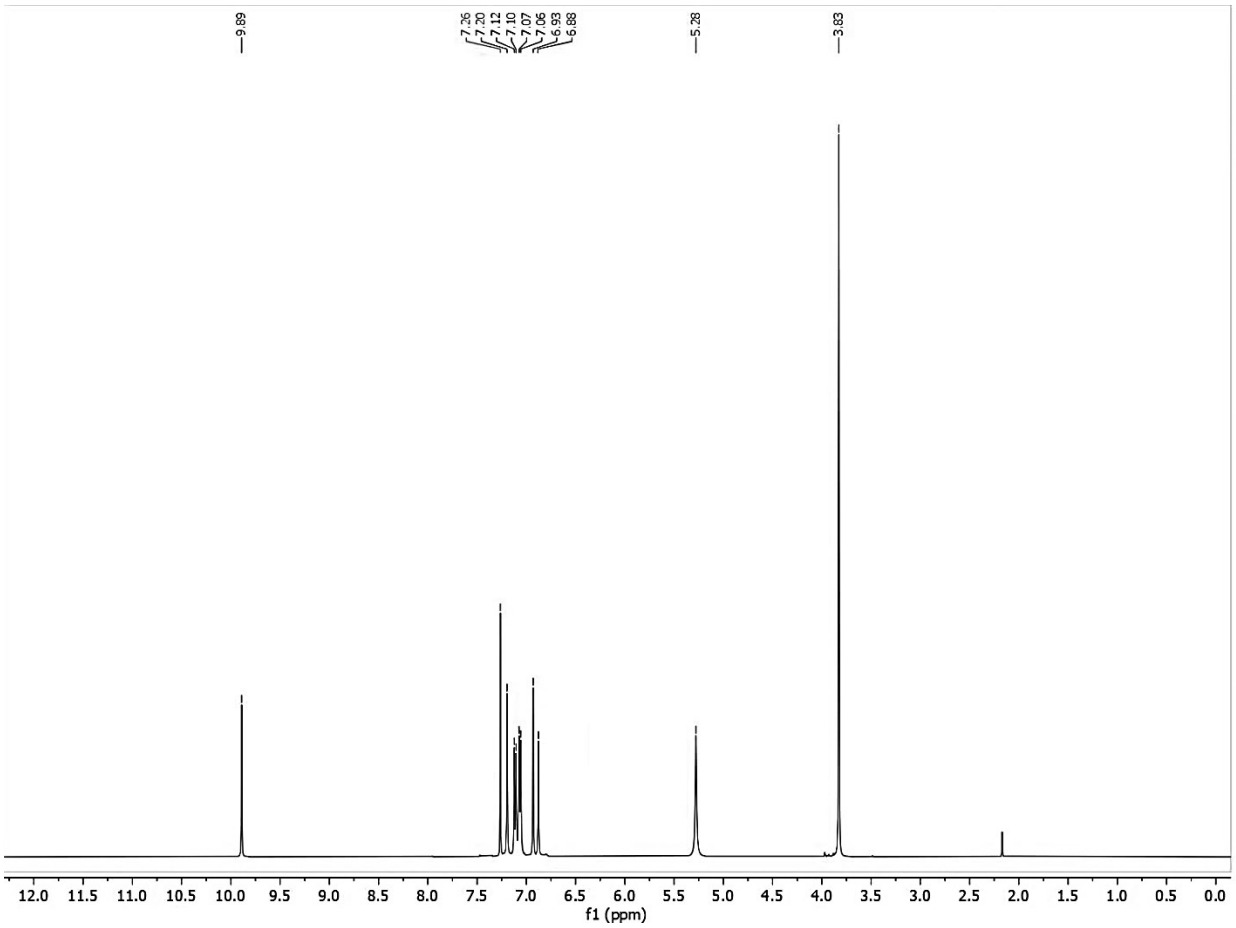

Figure S_1. ^{1}H-NMR of compound **C**.

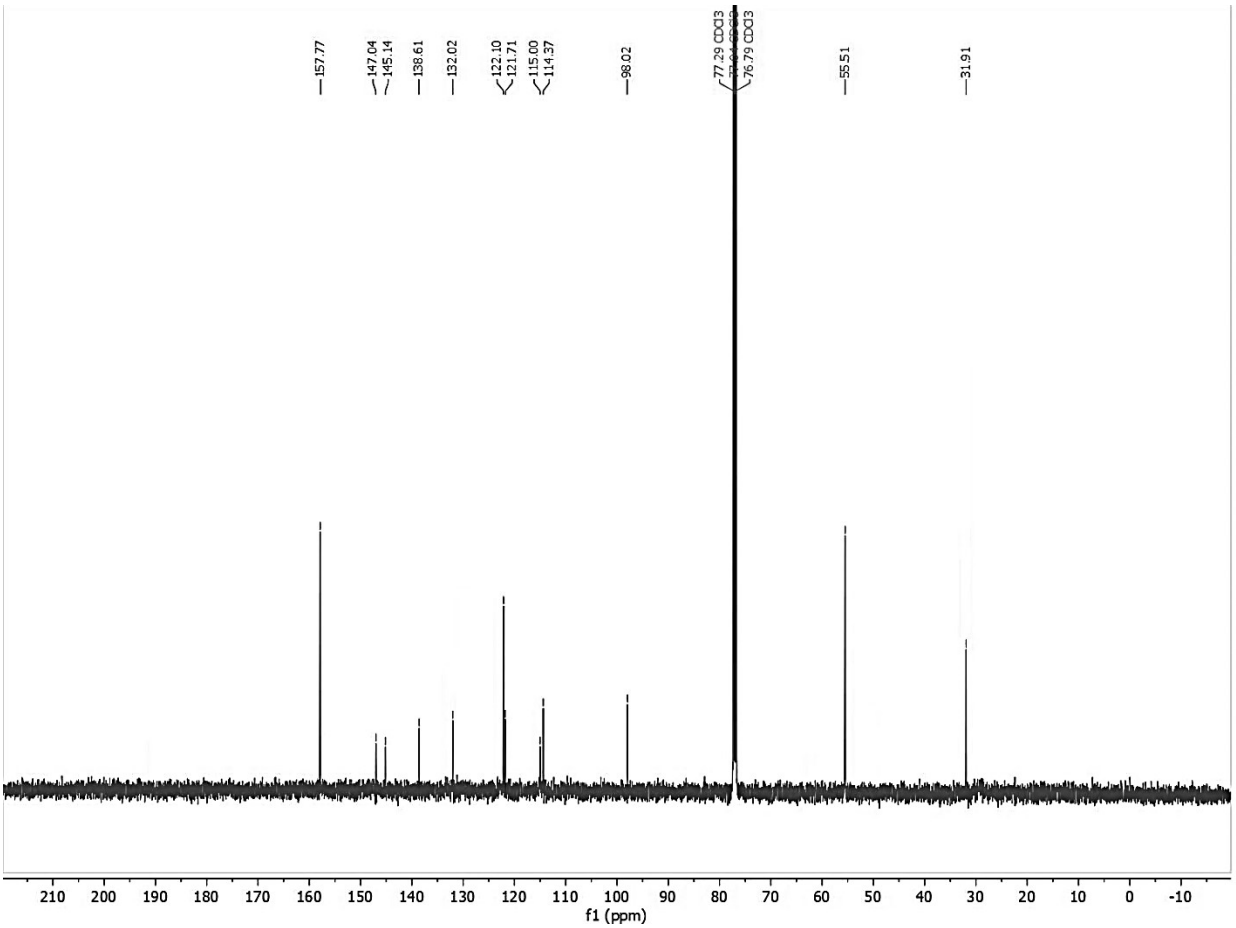

Figure S_2. ^{13}C-NMR of compound **C**.

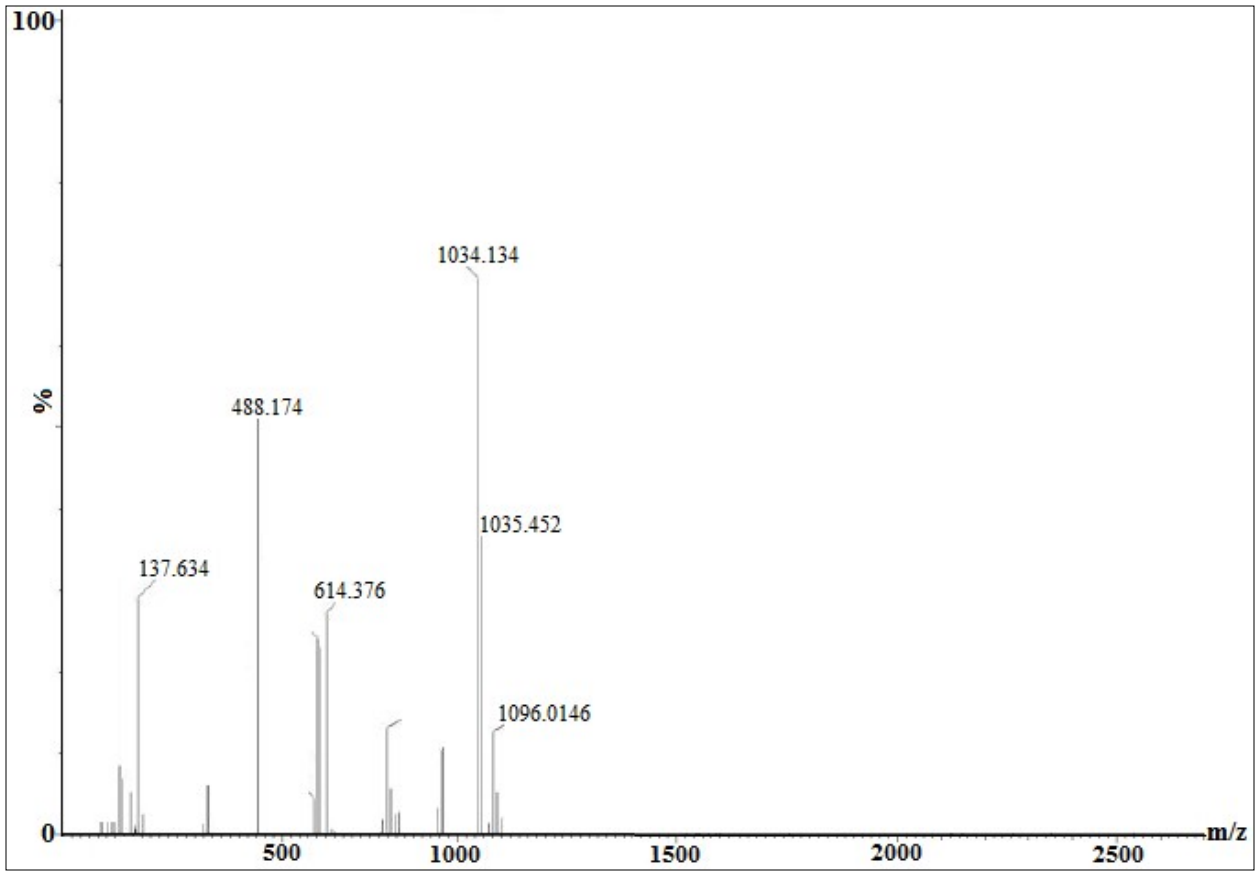

Figure S_3. HRMS of compound C.

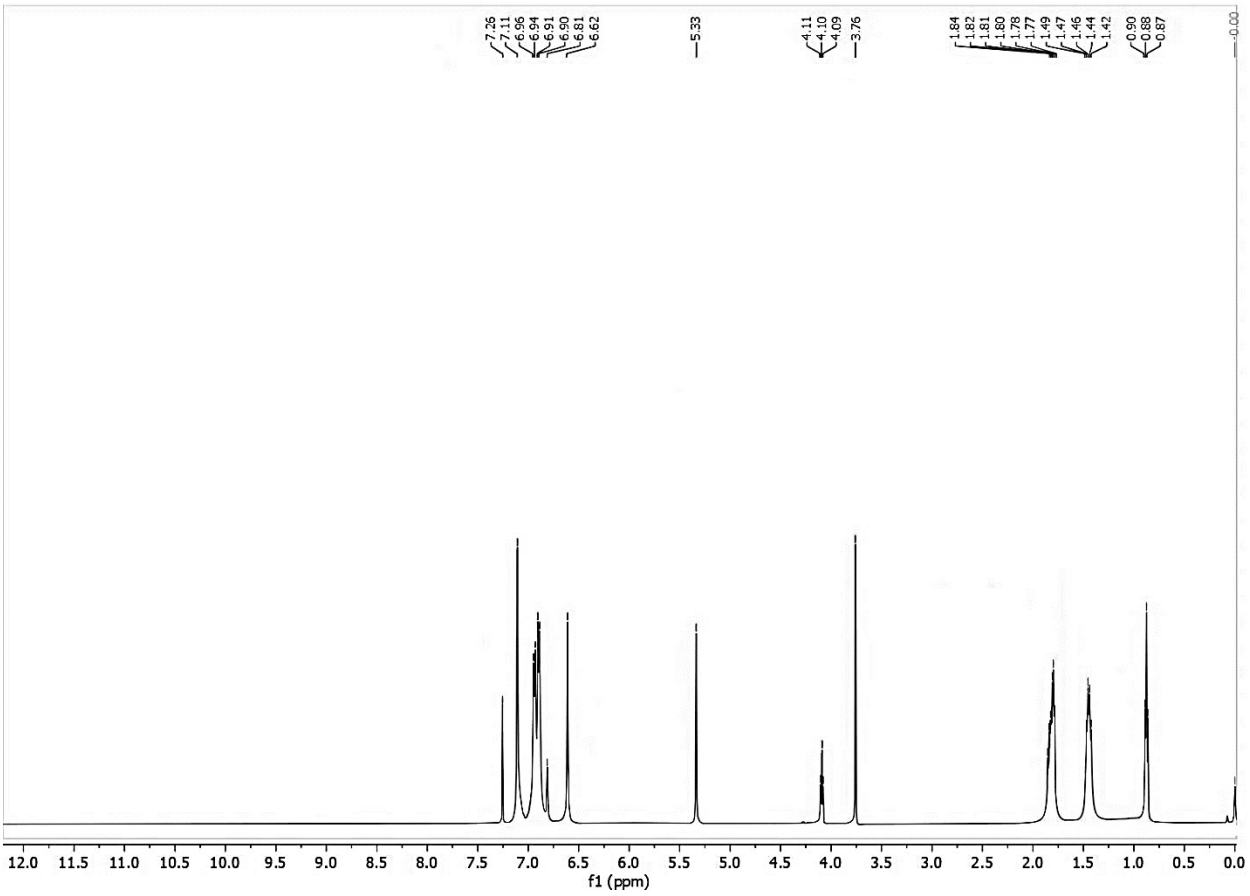

Figure S_4. ^{1}H-NMR of compound $\mathbf{D_1}$.

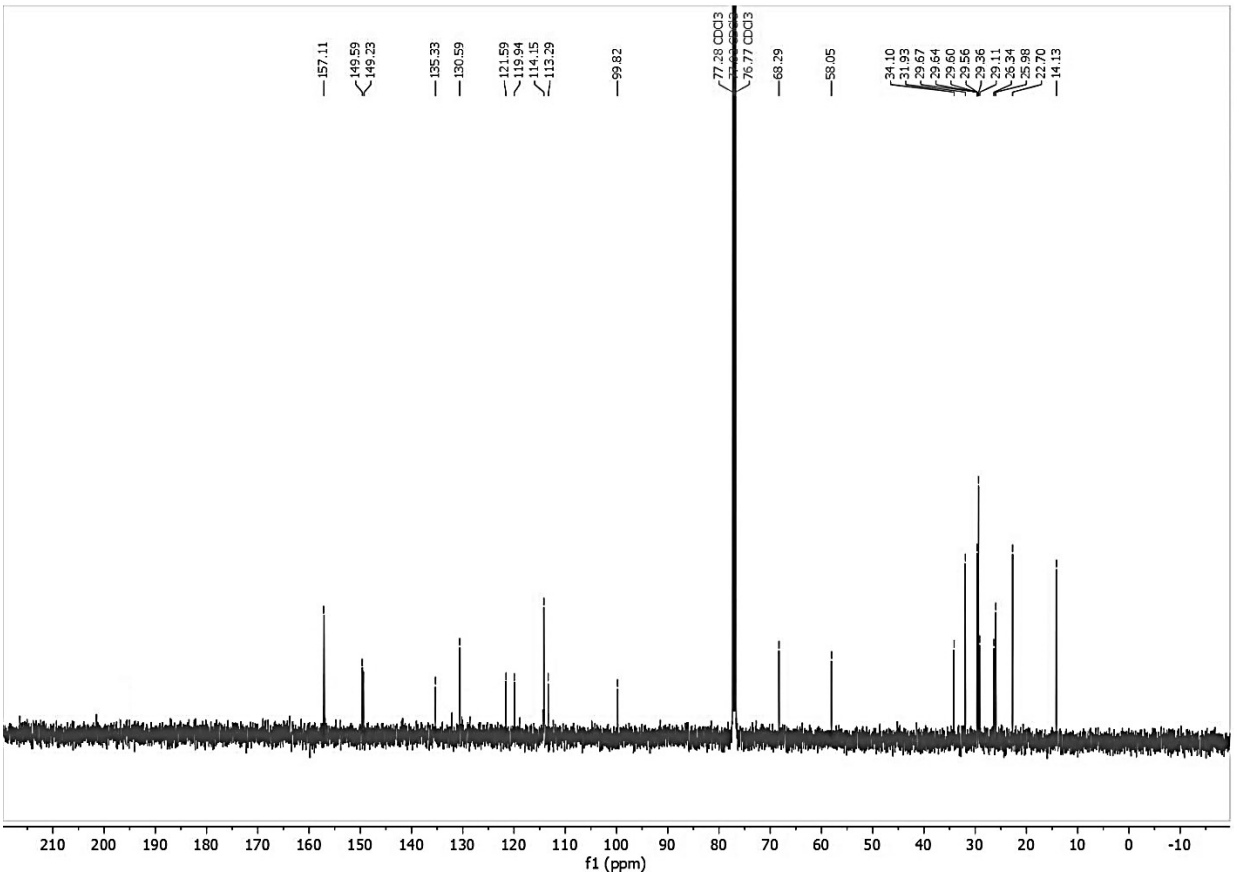

Figure S_5. ^{13}C-NMR of compound $\mathbf{D_1}$.

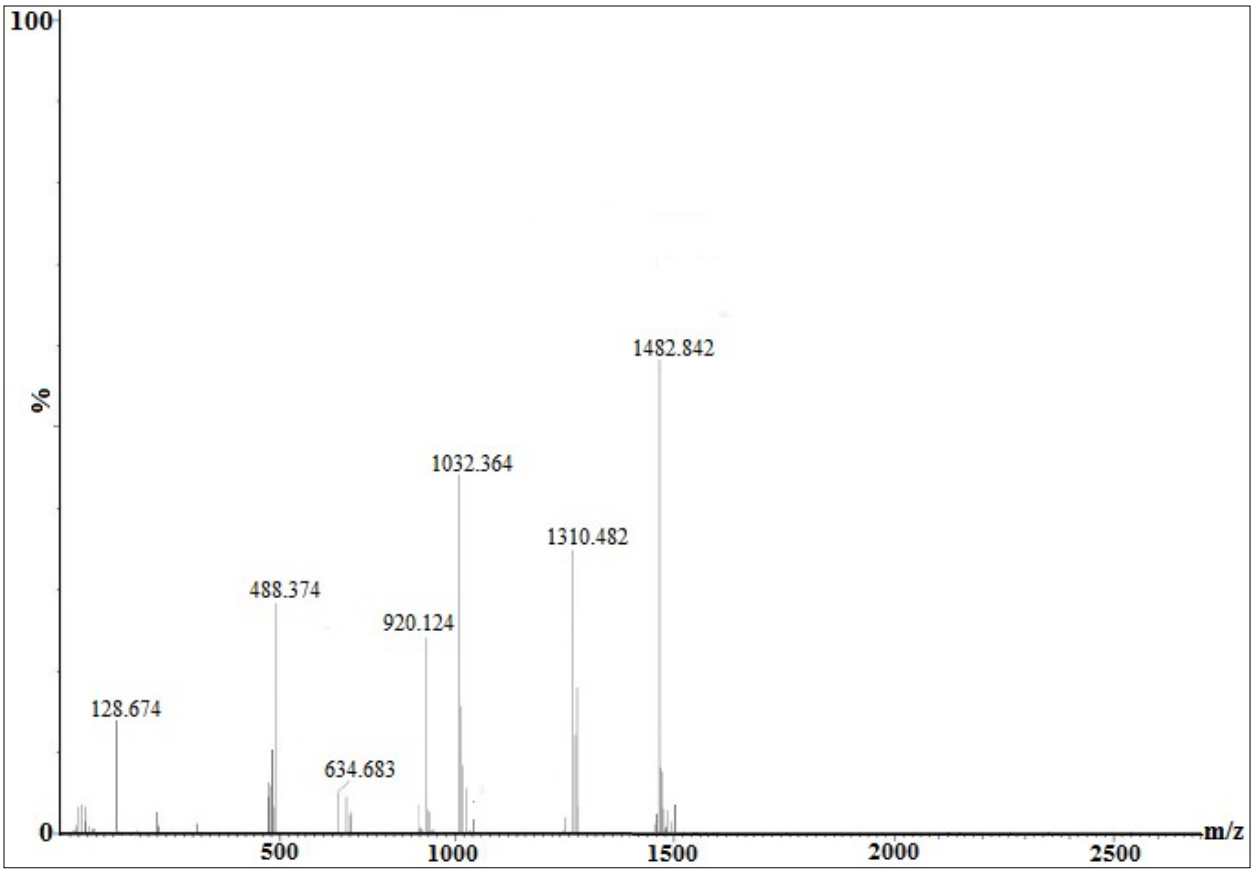

Figure S_6. HRMS of compound **D_1**.

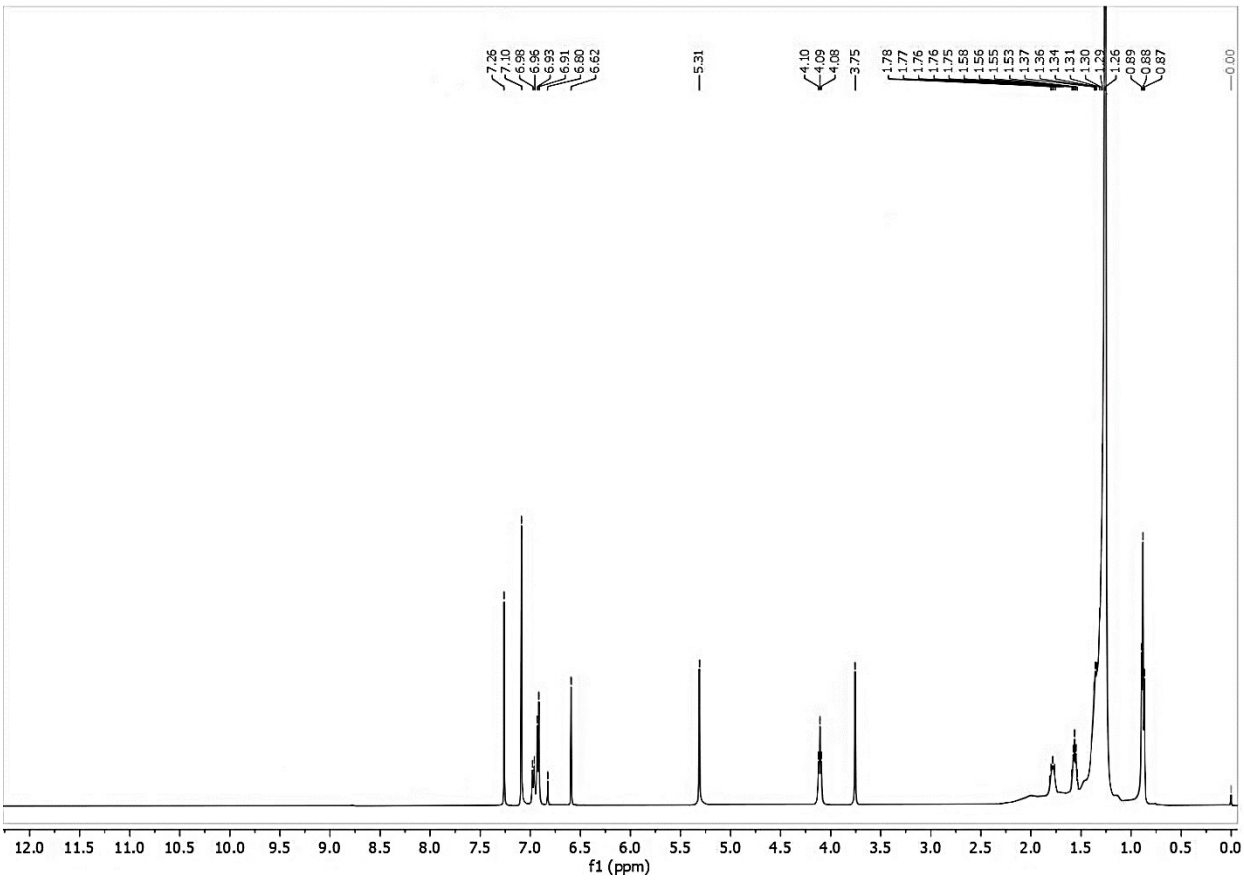

Figure S_7. ^{1}H-NMR of compound $\mathbf{D_2}$.

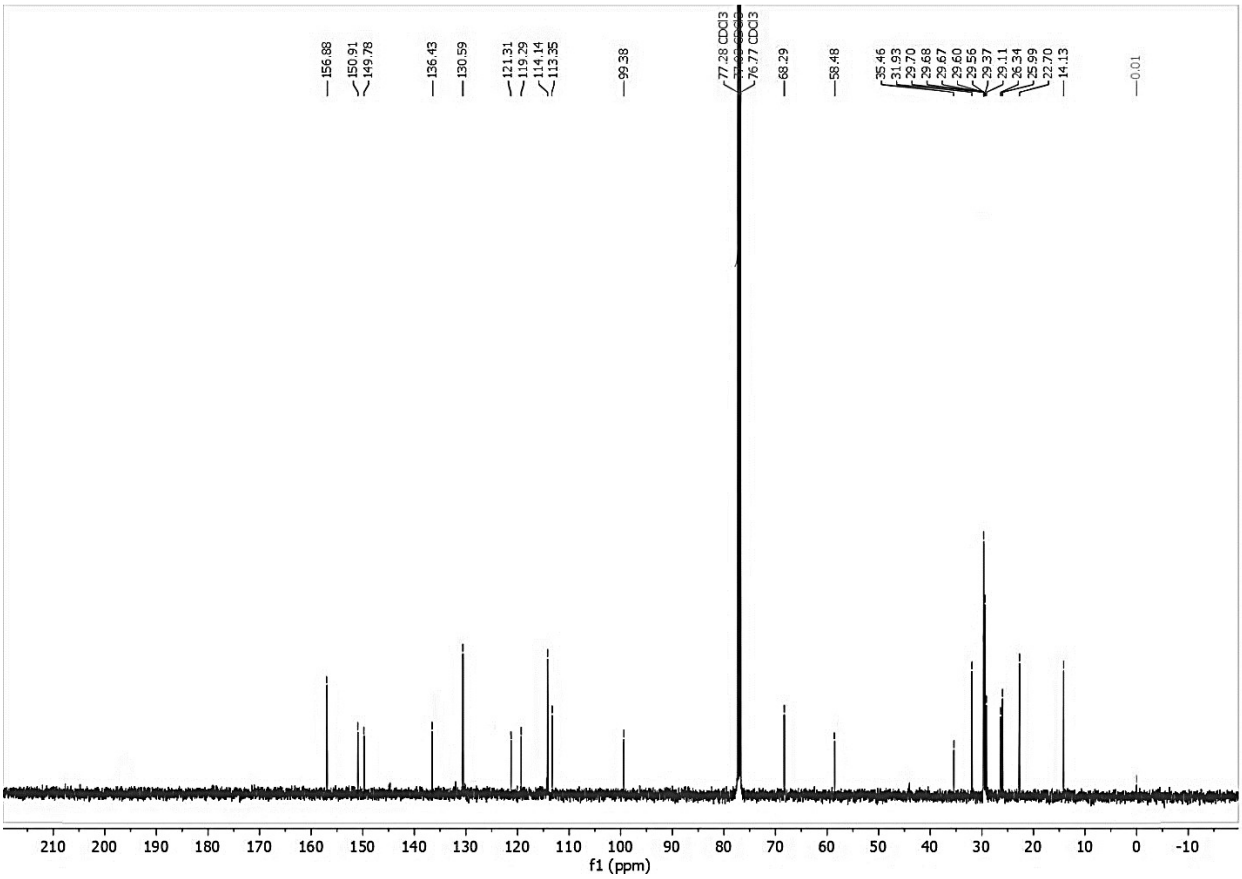

Figure S_8. ^{13}C-NMR of compound $\mathbf{D_2}$.

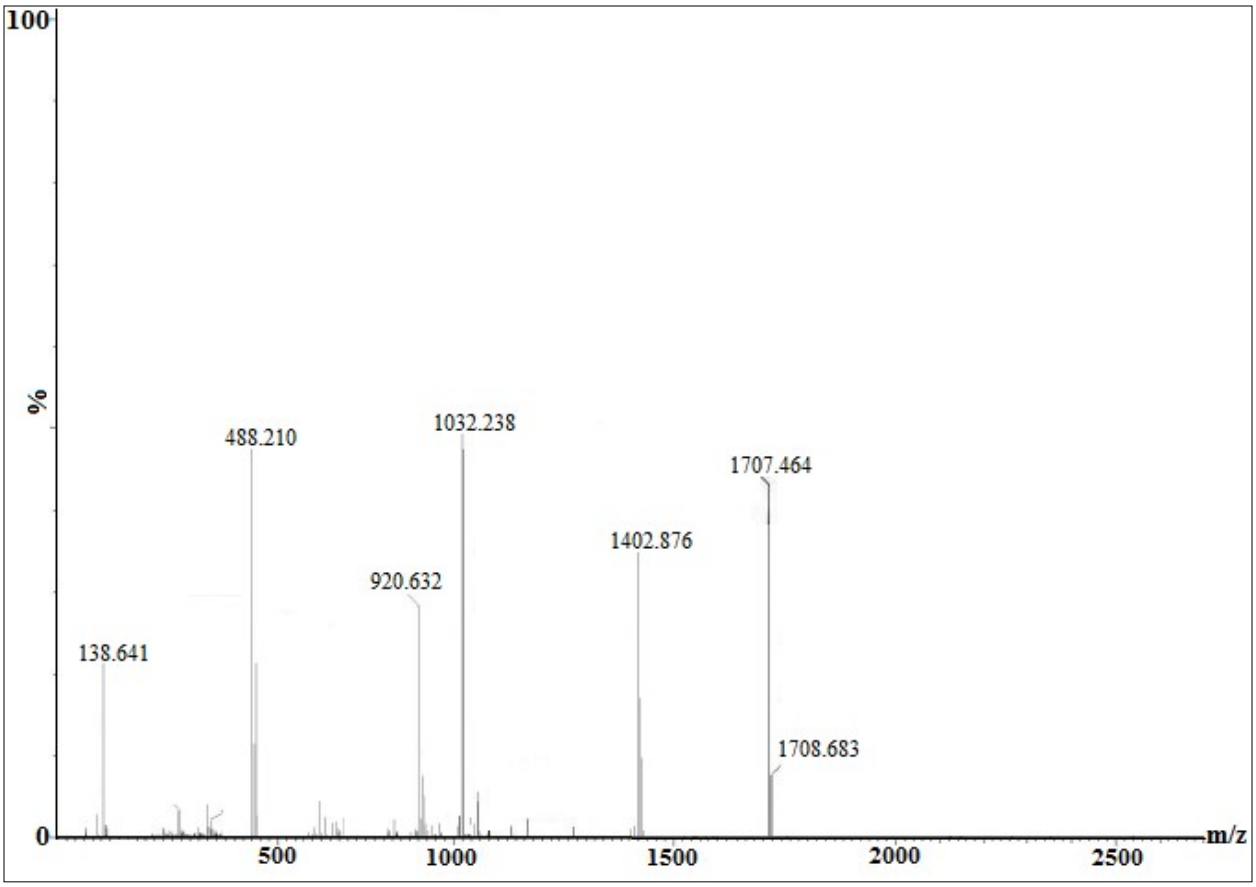

Figure S_9. HRMS of compound **D_2**.

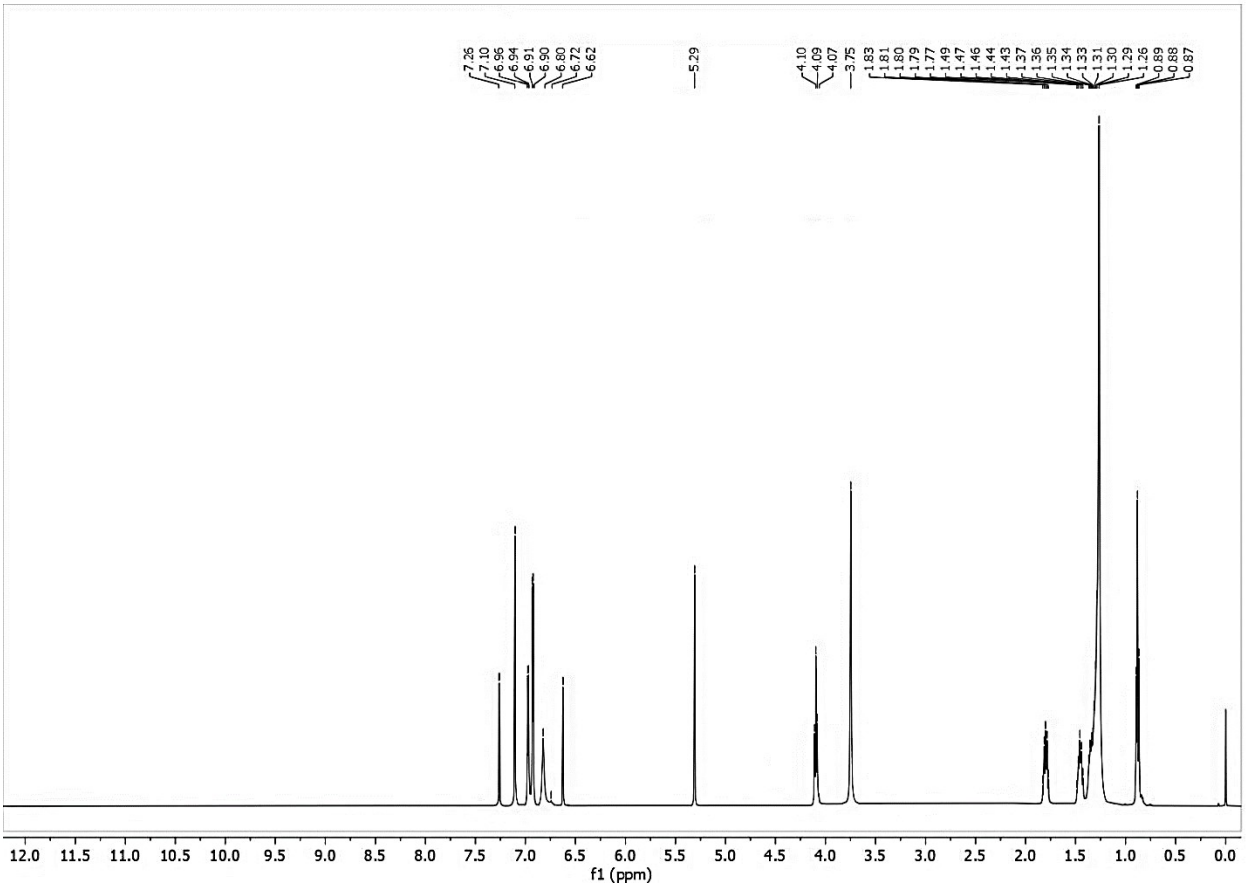

Figure S_{10}. ^{1}H-NMR of compound **D_3**.

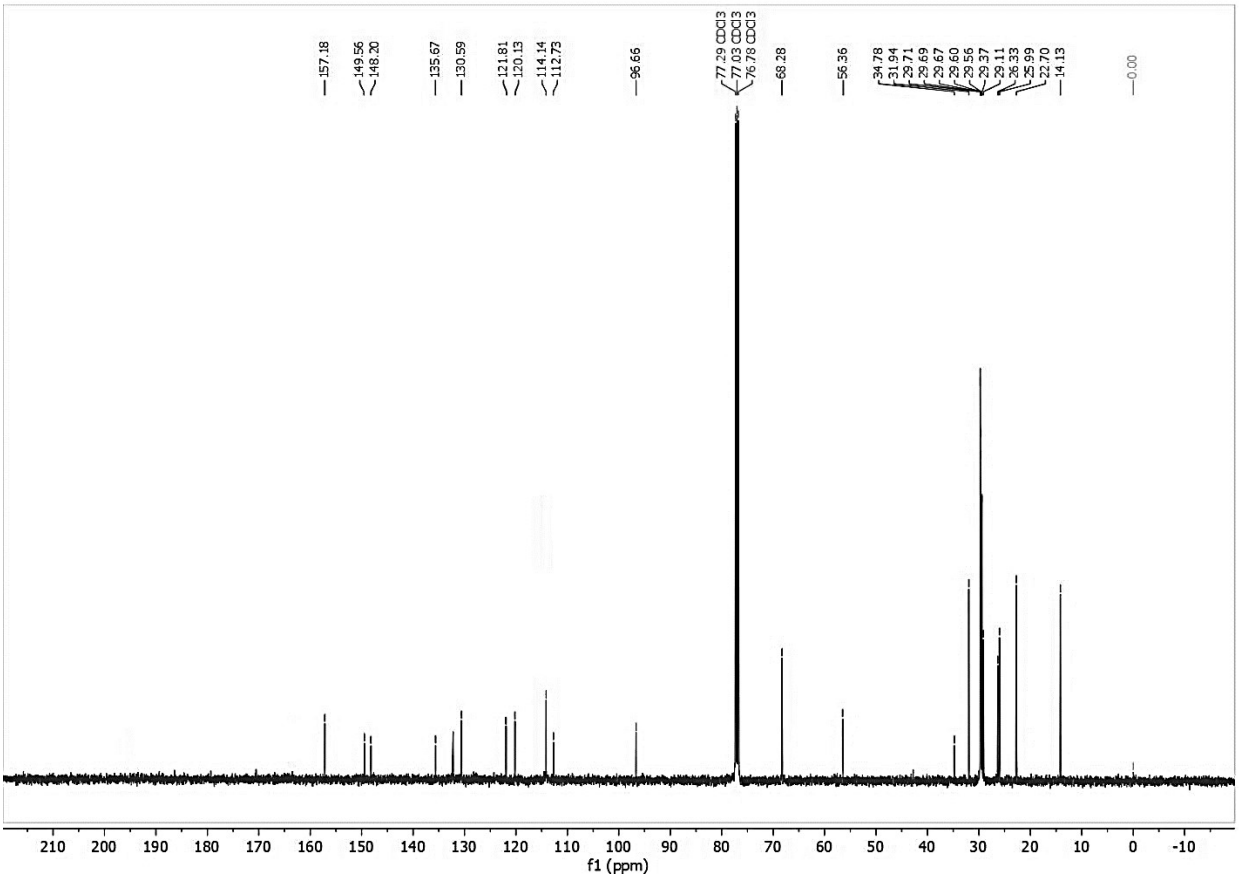

Figure S_{11}. ^{13}C-NMR of compound **D_3**.

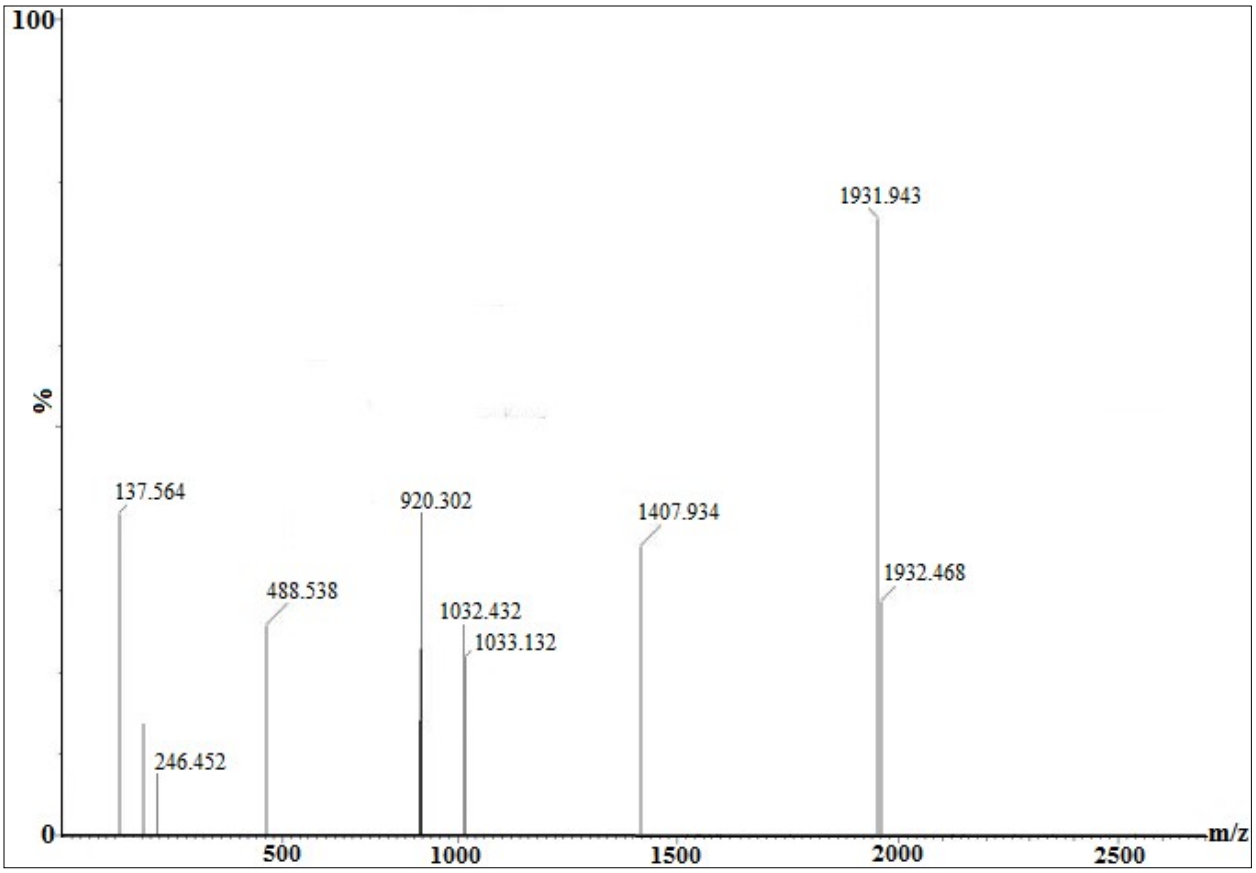

Figure S_{12}. HRMS of compound **D_3**.

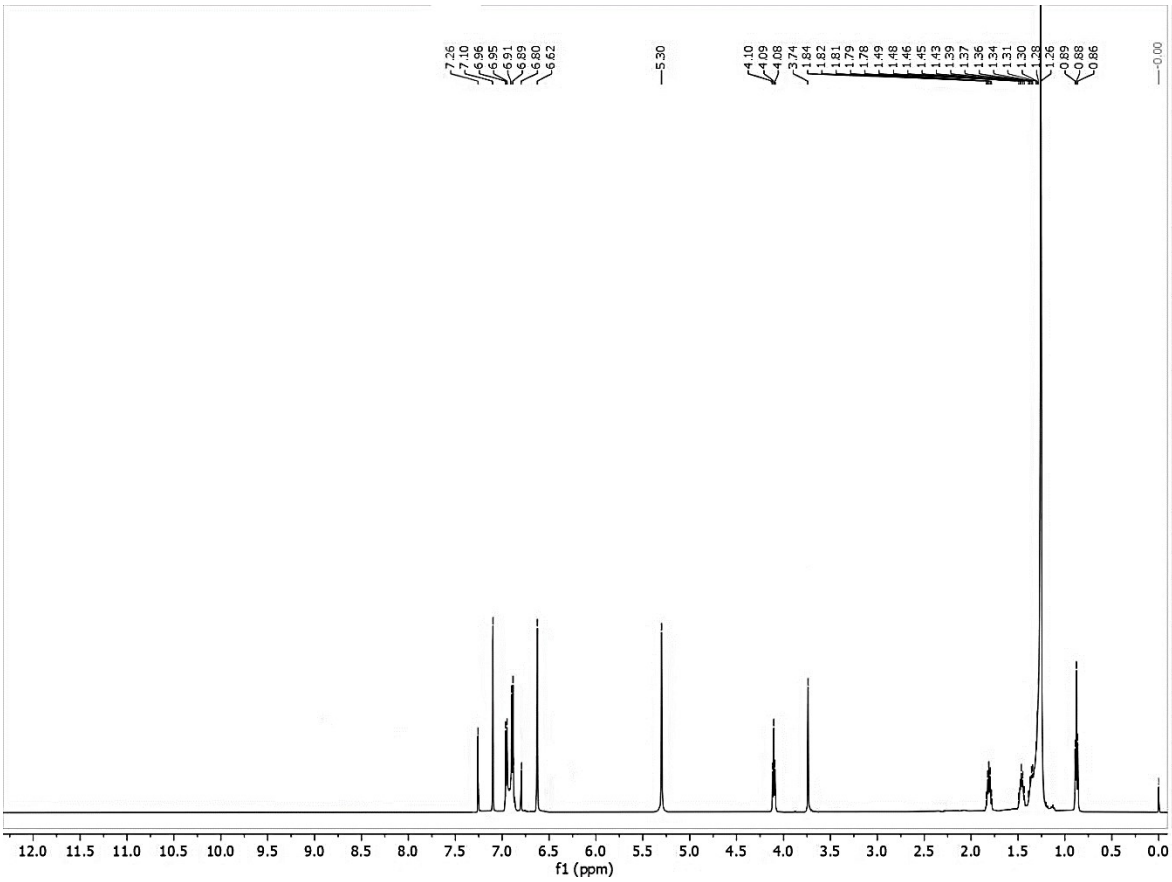

Figure S_{13}. ^{1}H-NMR of compound **D_4**.

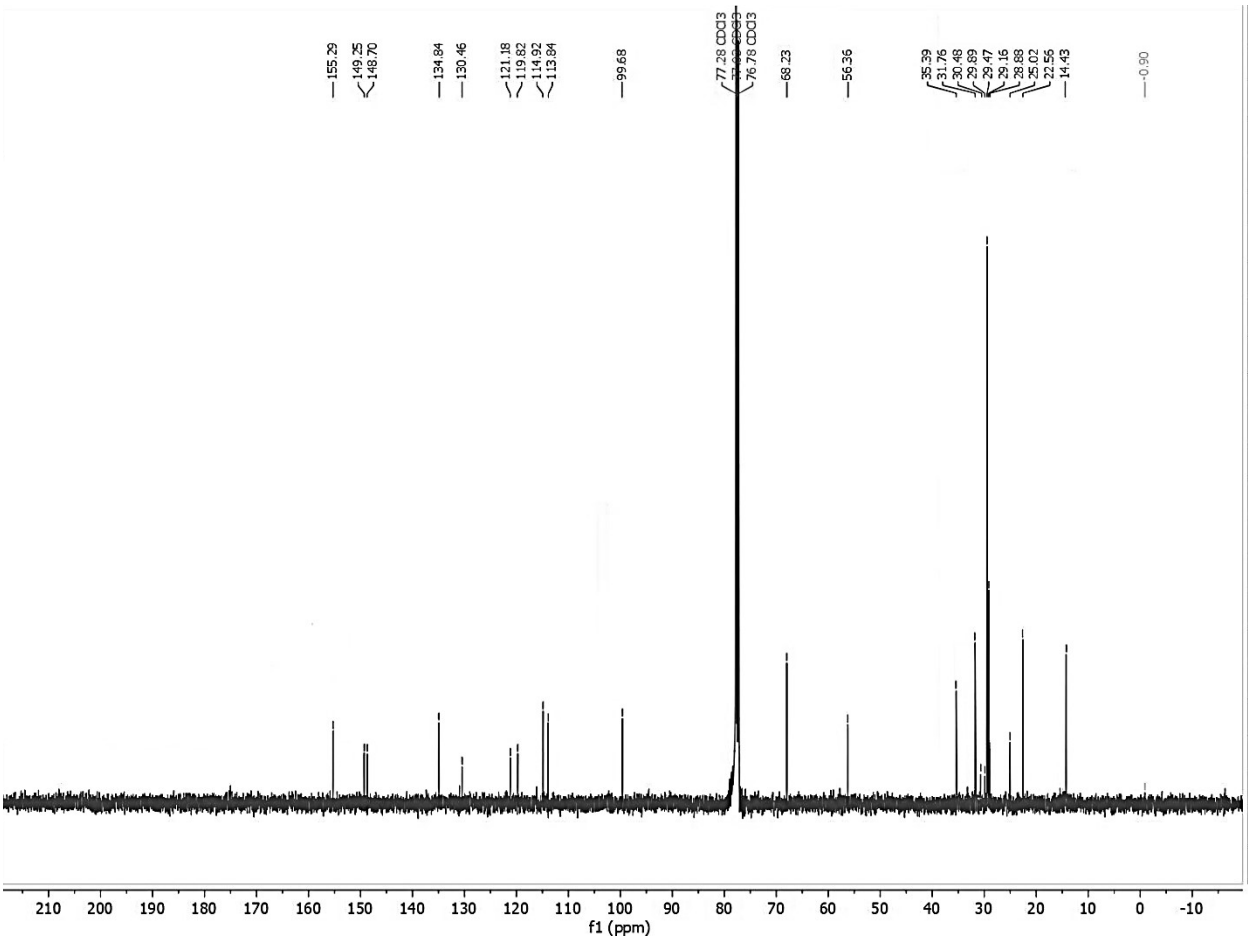

Figure S_{14}. ^{13}C-NMR of compound **D_4**.

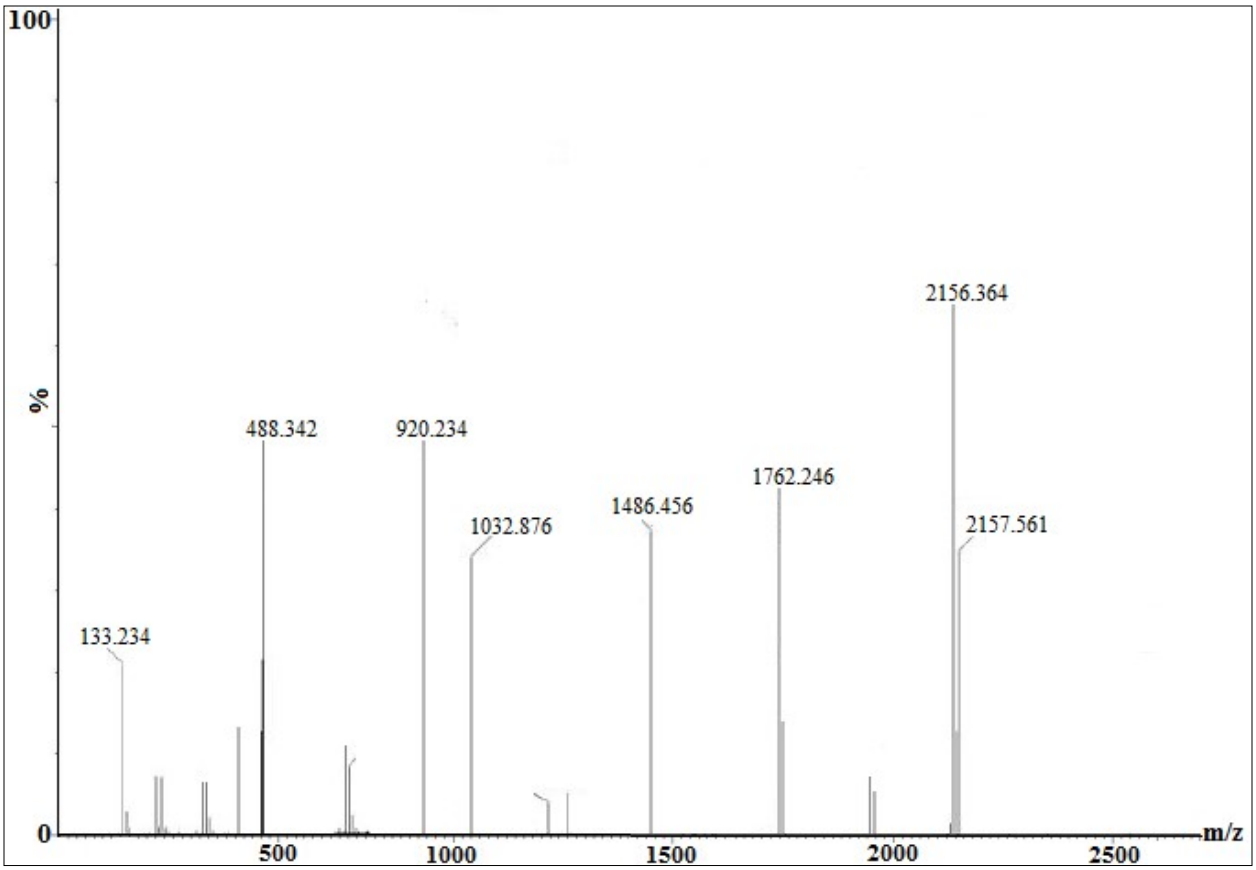

Figure S_{15}. HRMS of compound **D_4**.

References

1. D.Moore, G.W.Watson, T.Gunnlaugsson and S.E.Matthews. *New J.Chem*., **2008**, 32(6), 994.

2. F.Potet, A.N.Lorinc, S.Chaigne, C.R. Hopkins et al. *J.Bio.Chem.*, **2012**, 287(47), 39613.