Supplementary material (ESI) for Chemical Communications

SUPPLEMENTARY MATERIAL

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General. All reactions were carried out under a nitrogen atmosphere in flame dried glassware. **Commercially available reagents:** Acetic anhydride, mesyl chloride, isobutyryl chloride, *p*-anisoyl chloride, and 4-(N,N-dimethyl)-amino-pyridine (DMAP) were purchased from Acros Chemical Co. and were used without further purification. Triethyl amine was distilled from calcium hydride under a nitrogen atmosphere and allowed to stand over potassium hydroxide. Tetrahydrofuran was distilled from sodium benzophenone ketyl under a nitrogen atmosphere. **Thin Layer Chromatography:** Whatman silica gel 60 Å with fluorescent indicator, 250 micrometer thickness glass backed with hexanes/ethyl acetate as the mobile phase. **Instrumental Analyses:** NMR: Spectra were recorded on a Varian 360 MHz, and an Inova 500 MHz in $CDCl_3$ containing 0.03% TMS. Chemical shifts are listed downfield in ppm relative to tetramethylsilane. Coupling constants are given in Hz. **Mass Spectrometry:** Analysis was performed on a Bruker Autoflex MALDI-TOF MS with DHB as the matrix.

Synthesis of Octaesters. Representative Procedure.
To a solution of 100 mg (0.0343 mmol) of octol **2** in 6.86 mL of dry THF is added 0.086 mL of triethylamine, 0.026 mL of acetic anhydride, and a crystal of DMAP (cat. amount). The reaction mixture was stirred for one hour, after which time TLC analysis (hex/EtOAc 1:1) showed complete consumption of the starting material. The THF was removed *in vacuo* and the residue was partitioned between methylene chloride (30 mL) and water (10 mL). The aqueous layer was extracted with methylene chloride 2x (30 mL) and the combined organic layers were washed with brine (30 mL) dried over sodium sulfate and concentrated *in vaccuo* to give 61 mg (99%) of **4** as a white powder. To ensure removal of water the octaester was dissolved in dry THF and dry toluene, sequentially, followed by repeated distillation of the solvent through a Vigorex column. Samples were then dried under heated vacuum overnight prior to NMR acquisitions. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, 12 H, CH_3), 1.17 (s, 12 H, CH_3 α to prochiral center) 1.31 (m, 32 H, $CH_2CH_2CH_2CH_2$), 1.43-1.54 (m, 24 H, $OCOCH_3$) 2.23 (m, 8 H, CH_2 α to methine), 4.04 (s, 16 H, CH_2 α to prochiral center) 4.14 (d, 4 H inner OCH_2, J = 7.32 Hz) 4.78 (t, 4 H, methine, J = 7.8 Hz) 5.04 (s, 8 H, CH_2OCO) 5.78 (d, 4 H outer OCH_2, J = 7.32 Hz) 7.16 (s, 4 H, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.25, 17.86, 20.07, 22.84, 27.95, 29.62, 32.00, 36.97, 46.26, 56.88, 65.60, 100.15, 121.37, 122.74, 138.44, 154.43, 170.58, 172.59. HRMS (MALDI-TOF; M + Na^+) calcd for $C_{96}H_{128}O_{32}Na$ 1815.828, found 1816.114.

Octamesylate (6). White powder: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.92 (t, 12 H, CH_3), 1.19 (s, 12 H, CH_3 α to prochiral center) 1.31 (m, 32 H, $CH_2CH_2CH_2CH_2$), 1.39-1.54 (m, 24 H, $OCOCH_3$) 2.22 (m, 8 H, CH_2 α to methine), 4.06 (s, 16 H, CH_2 α to prochiral center) 4.13 (d, 4 H inner OCH_2, J = 7.2 Hz) 4.74 (t, 4 H, methine, J = 7.2 Hz) 5.06 (s, 8 H, CH_2OCO) 5.77 (d, 4 H outer OCH_2, J = 7.2 Hz) 7.10 (s, 4 H, ArH); ^{13}C NMR (360 MHz, $CDCl_3$) δ 13.94,

17.35, 22.57, 27.70, 29.35, 29.81, 31.73, 36.59, 36.80, 46.62, 57.16, 69.04, 99.78, 121.06, 122.72, 138.66, 154.24, 170.88. HRMS (MALDI-TOF; M + Na^+) calcd for $C_{88}H_{128}O_{40}S_8Na$ 2103.56, found 2105.392.

Octaisopropionate (7). White powder: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, 12 H, CH_3), 1.03 (d, 48 H, $CH(CH_3)_2$ 1.22 (s, 12H, CH_3 α to prochiral center) 1.31 (m, 32 H, $CH_2CH_2CH_2CH_2$), 2.24 (m, 8 H, CH_2 α to methine), 2.45 (sep, 8 H, CH α to $(CH_3)_2$), 4.12- 4.20 (m, 16 H, CH_2 α to prochiral center, 4 H inner OCH_2) 4.68 (t, 4 H, methine, J = 7.7 Hz) 5.04 (s, 8 H, CH_2OCO) 5.79 (d, 4 H outer OCH_2, J = 7.0 Hz) 7.18 (s, 4 H, ArH); ^{13}C NMR (500 MHz, $CDCl_3$) δ 13.57, 17.40, 18.27, 22.19, 27.31, 29.00, 29.61, 29.82, 31.34, 33.41, 36.34, 45.98, 56.61, 64.59, 99.15, 120.87, 120.98, 137.81, 153.76, 172.26, 175.85. HRMS (MALDI-TOF; M + Na^+) calcd for $C_{112}H_{160}O_{32}Na$ 2041.174 found 2040.099.

Octa *p*-methoxybenzoate (8). White powder: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.88 (t, 12 H, CH_3), (m, 12 H, CH_3 α to prochiral center, 32 H, $CH_2CH_2CH_2CH_2$), 1.25-1.43 (m, 24 H, $OCOCH_3$) 2.18 (m, 8 H, CH_2 α to methine), 3.82 (s, 24 H, $ArOCH_3$) 4.27 (d, 4 H inner OCH_2, J = 7.13 Hz) 4.49 (s, 16 H, CH_2 α to prochiral center) 4.78 (t, 4 H, methine, J = 8.0 Hz) 5.01 (s, 8 H, CH_2OCO) 5.62 (d, 4 H outer OCH_2, J = 7.27 Hz) 6.87 (d, 16 H, ArH, J = 8.9 Hz) 7.16 (s, 4 H, ArH) 7.95 (d, 16 H, ArH, J = 8.61 Hz); ^{13}C NMR (360 MHz, $CDCl_3$) δ 13.63, 17.59, 22.27, 27.39, 28.94, 29.30, 29.96, 31.43, 36.49, 46.51, 55.12, 57.21, 65.44, 99.25, 113.27, 131.04, 137.800, 146.16, 154.00, 163.29, 165.79, 172.46. HRMS (MALDI-TOF; M + Na^+) calcd for $C_{144}H_{160}O_{40}Na$ 2552.039, found 2552.803.

Fig. 1 ^{13}C NMR Spectrum of octaacetate (4).

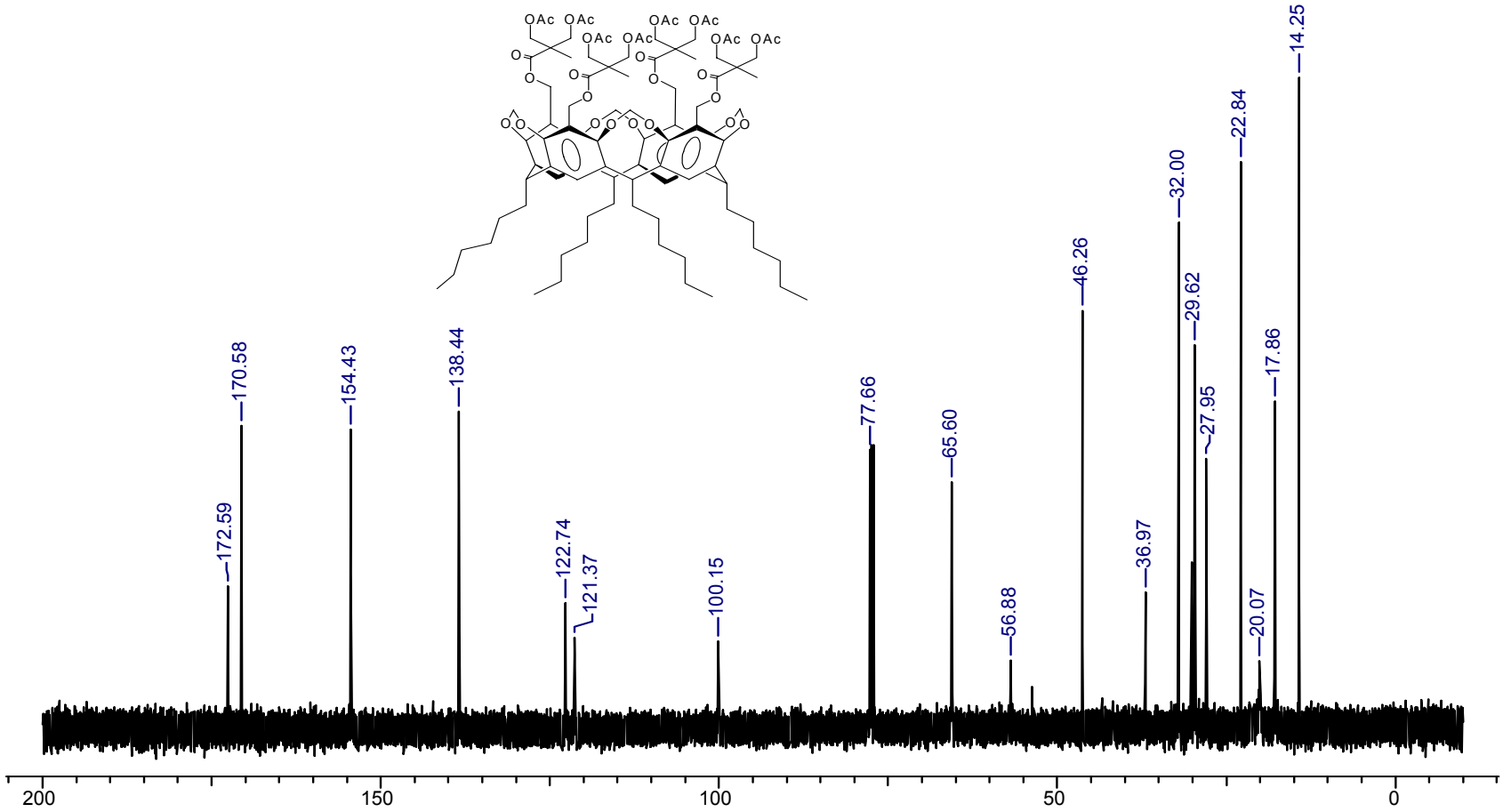

Fig. 2 MALDI- Mass spectrum of octaacetate (4).

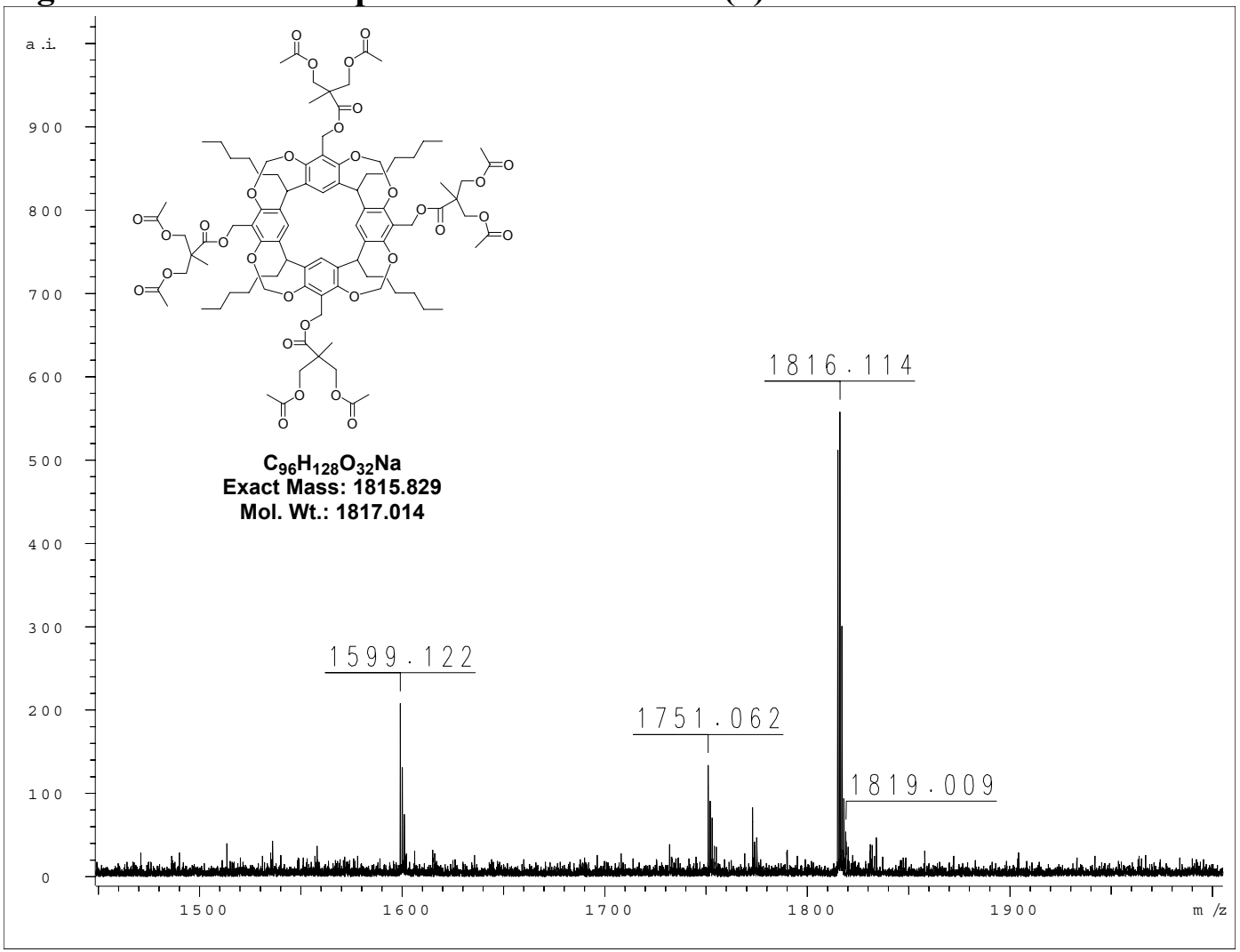

Fig. 3. ^{1}H- ^{1}H COSY Spectrum of Octol (2).

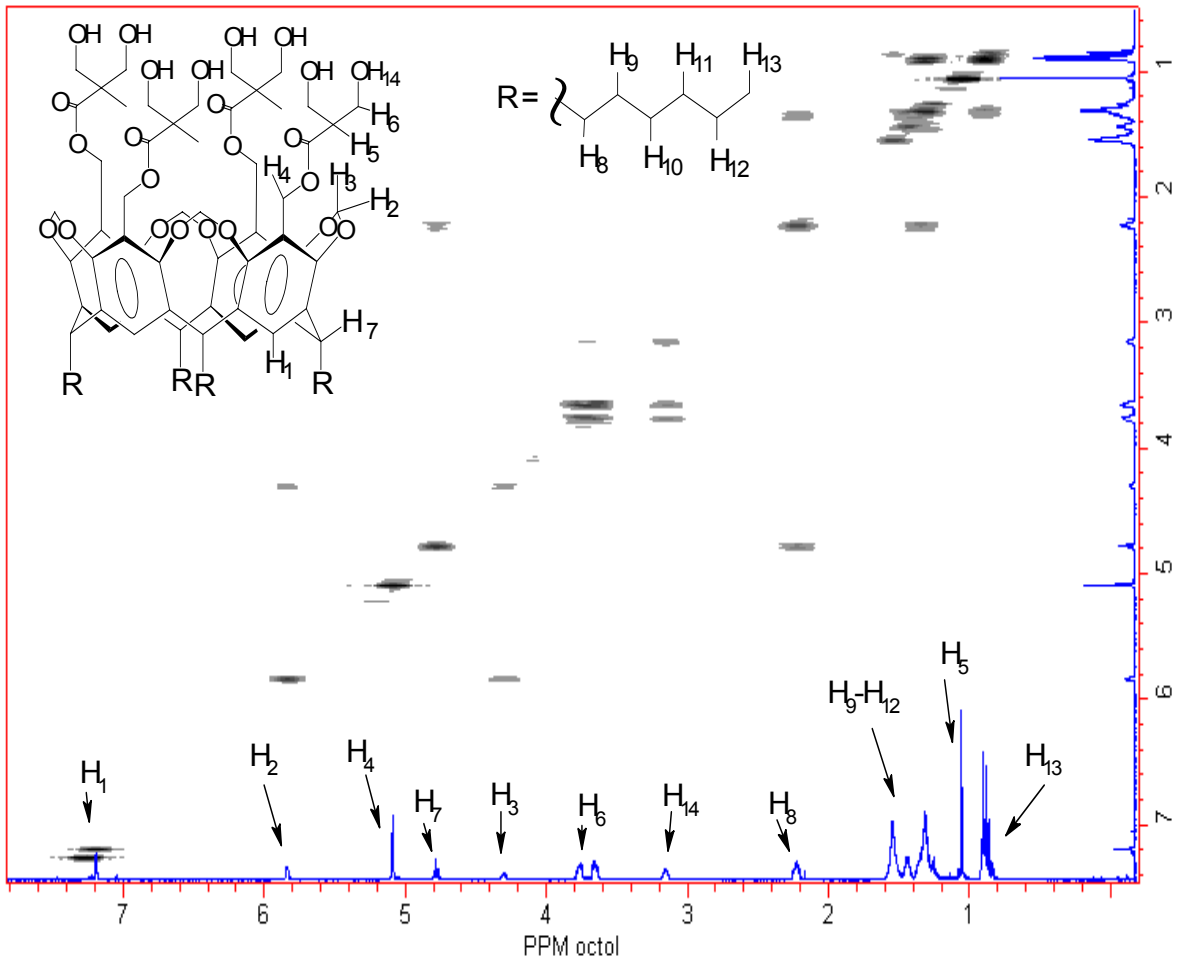

Fig. 4 ^{1}H- ^{1}H COSY Spectrum of Octaacetate (4).

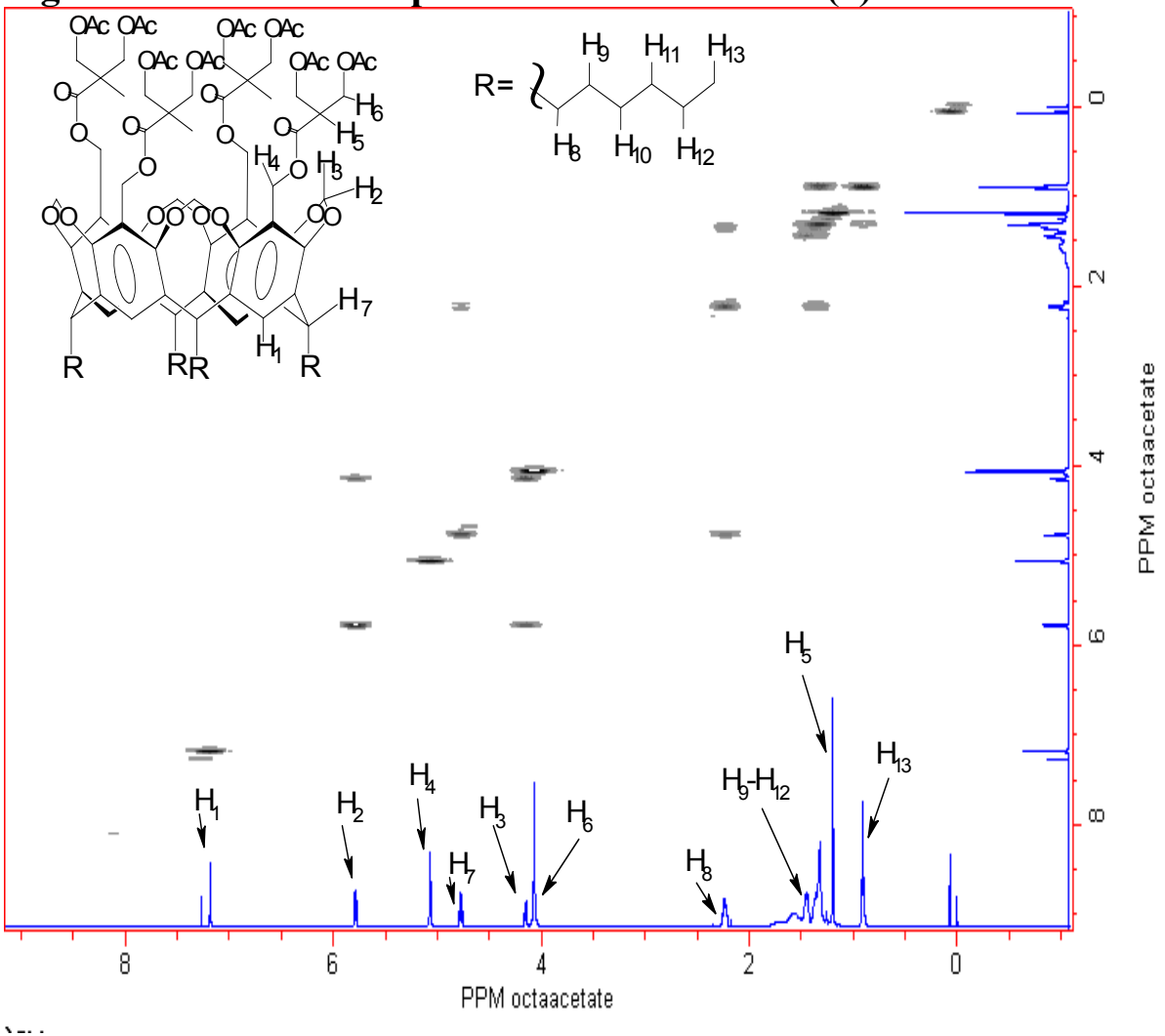

Fig. 5 ^{1}H NMR spectra of octaacetate (4) in $CDCl_3$; (a) at 20 ºC, (b) at 10 ºC, (c) at 0 ºC, (d) at -10 ºC, (e) at -20 ºC, (f) at -30 ºC, (g) at -40 ºC, (h) at -50 ºC.

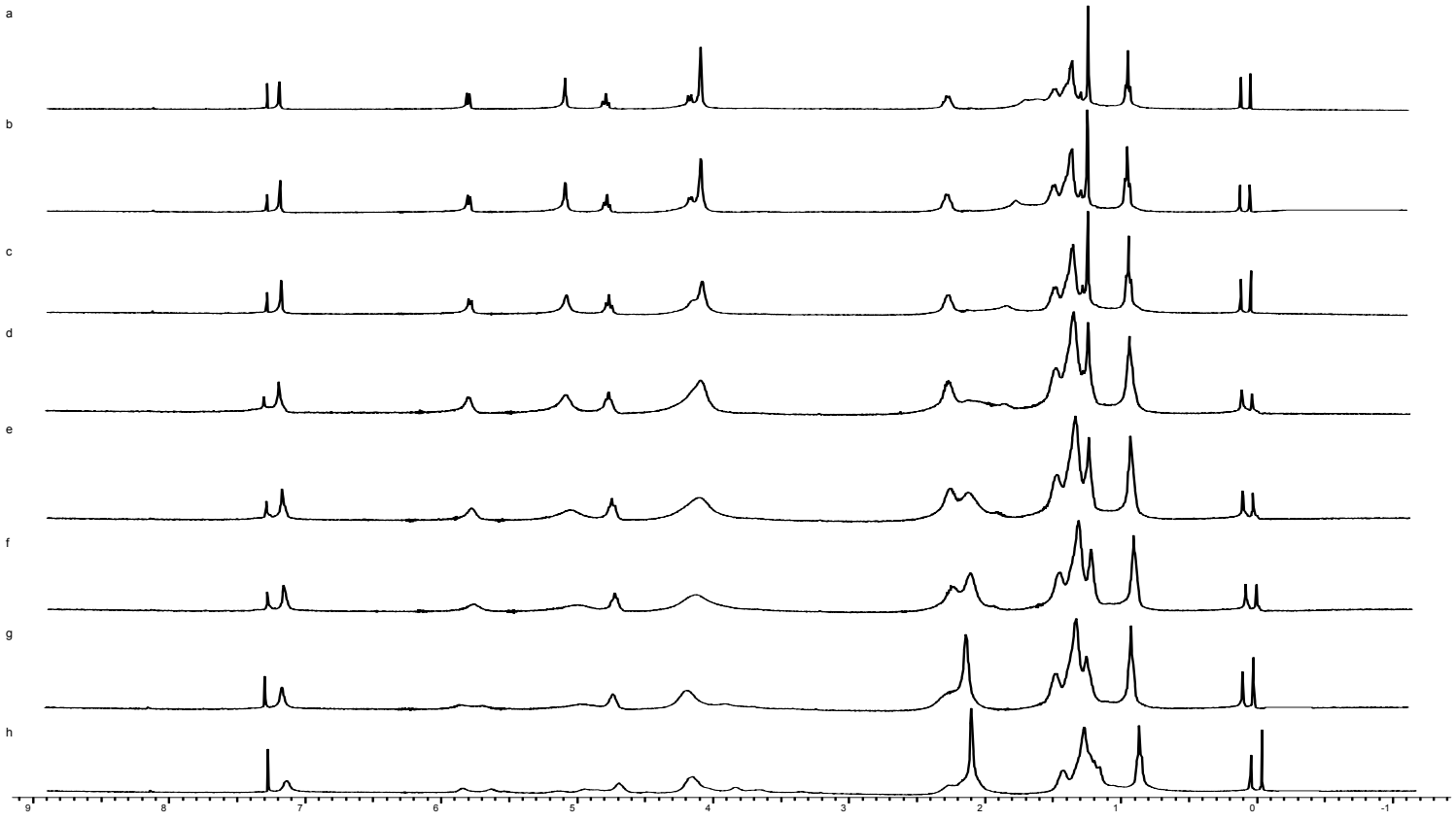

Fig. 6 ^{1}H NMR spectra of octaacetate (4) in DMSO-d_6 (0- 2.7 ppm) at 300, 320, 340, 360, and 380 K.

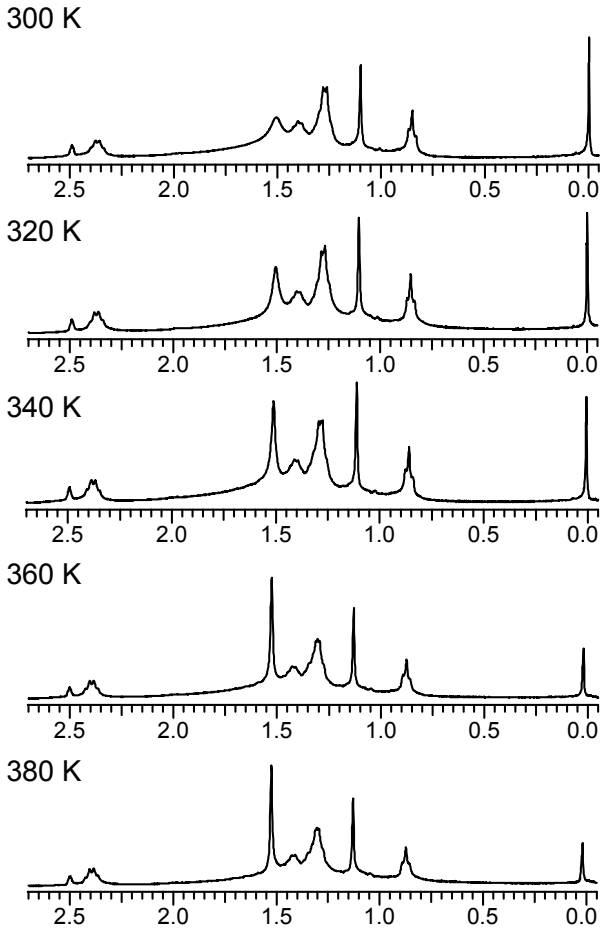

Fig. 7 ^{1}H NMR spectra of octamesylate (6) in $CDCl_3$; (a) at 20 ºC, (b) at 10 ºC, (c) at 0 ºC, (d) at -10 ºC, (e) at -20 ºC, (f) at -30 ºC, (g) at -40 ºC, (h) at -50 ºC.

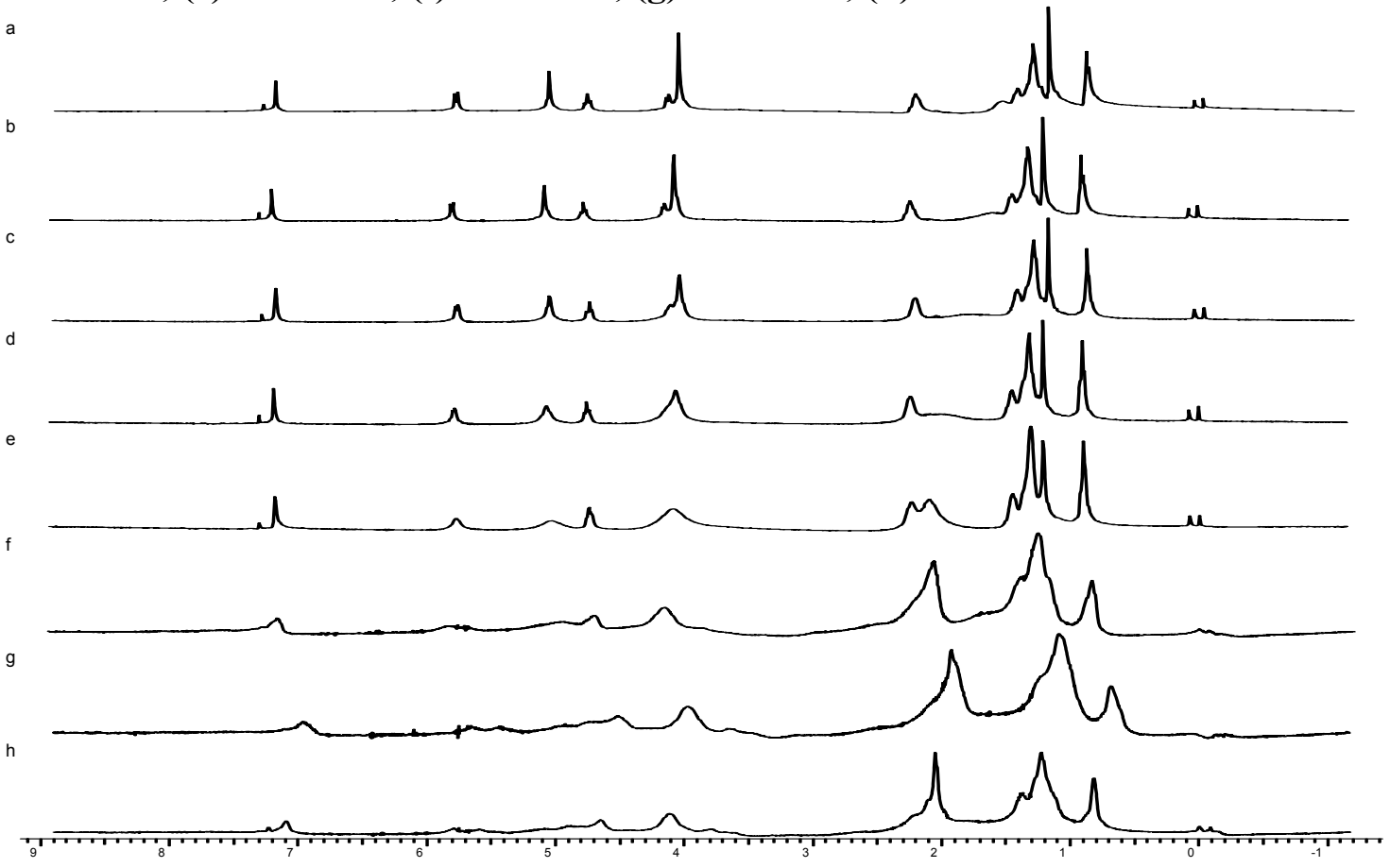

Fig. 8 ^{1}H NMR spectra of octaisopropionate (7) in $CDCl_3$; (a) at 20 ºC, (b) at 10 ºC, (c) at 0 ºC, (d) at -5 ºC, (e) at -15 ºC, (f) at -20 ºC.

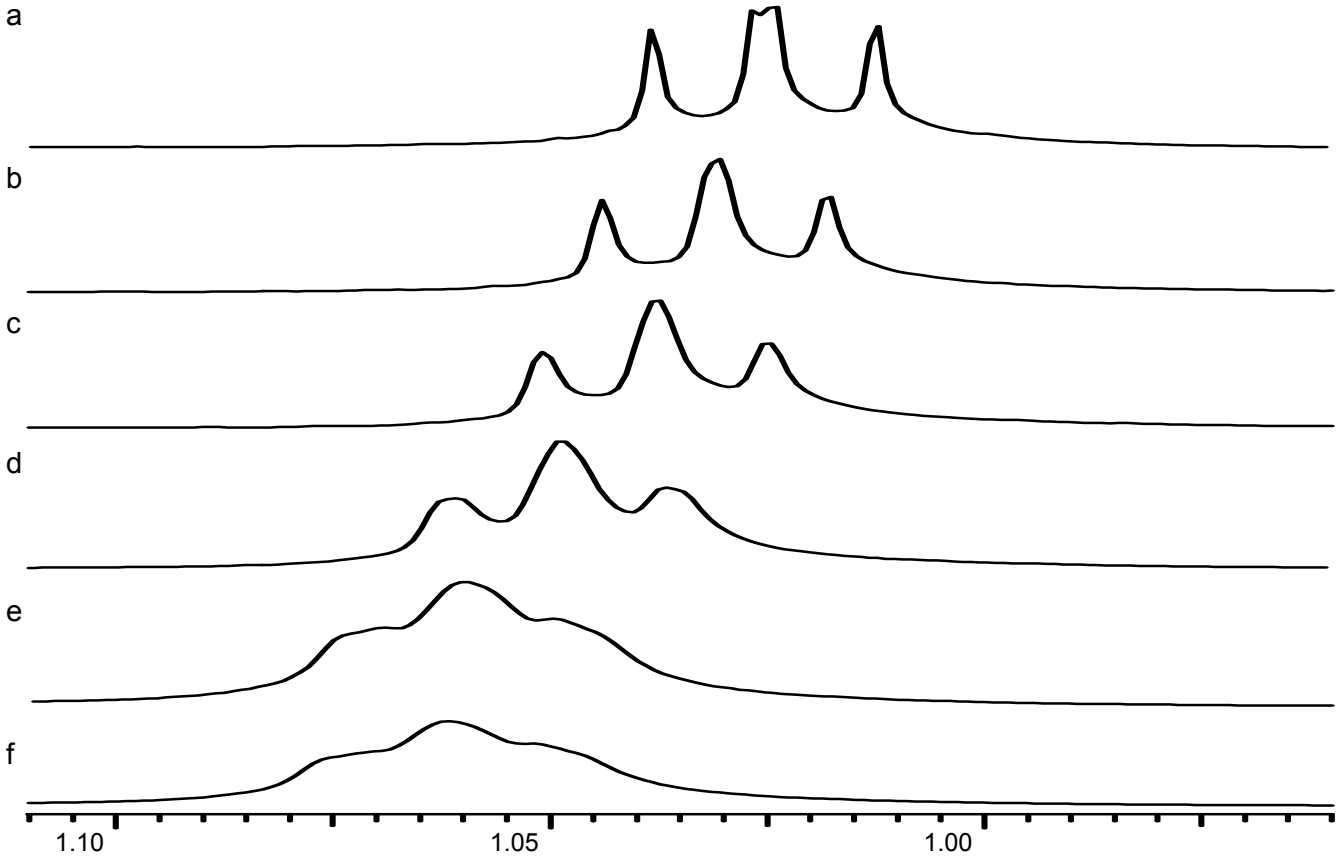

Fig. 9 250 MHz ^{1}H NMR Spectrum of octol (2) in $CDCl_3$.

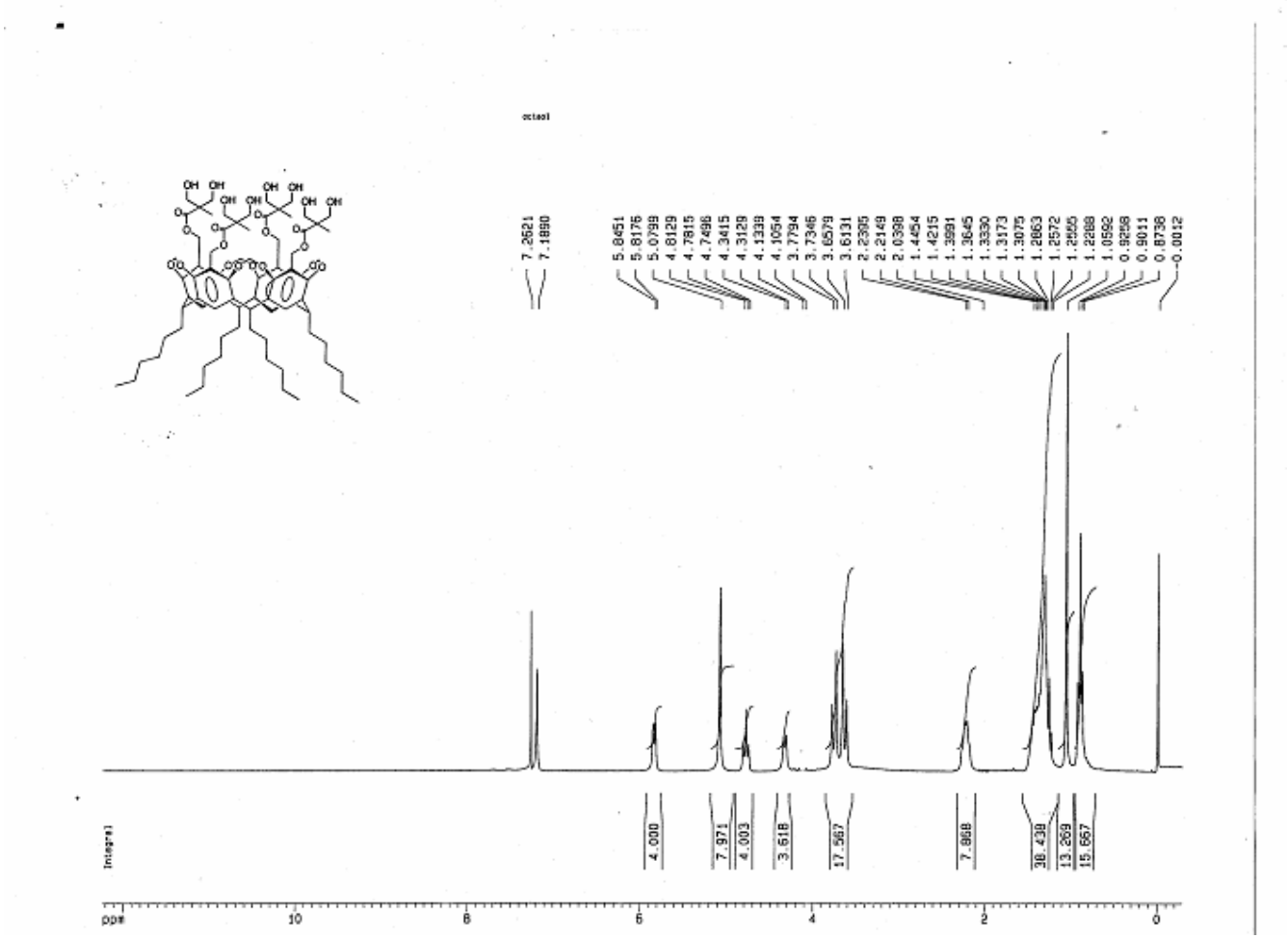

Fig. 10 62.5 MHz ^{13}C NMR Spectrum of octol (2) in $CDCl_3$.

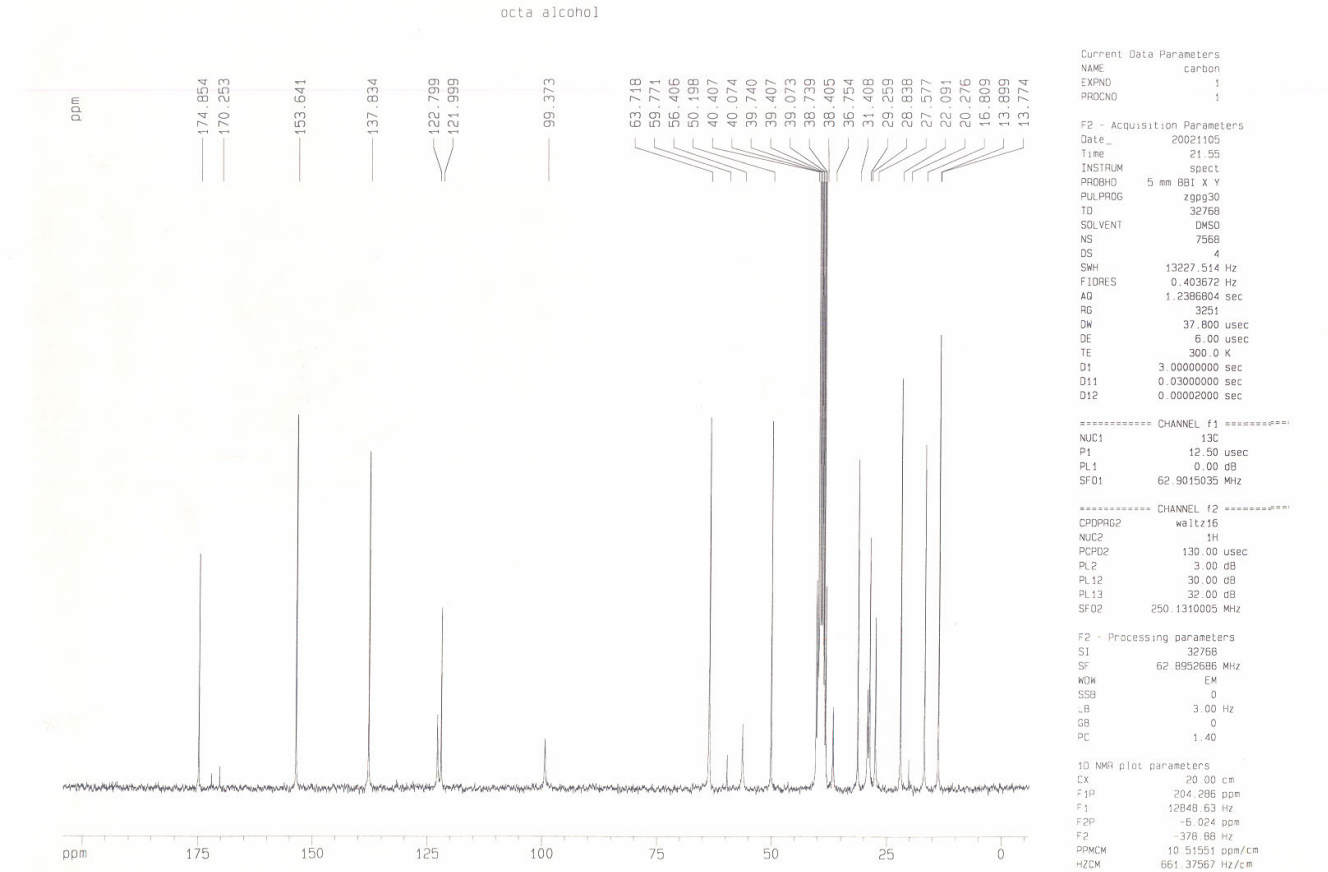

Fig. 11 MALDI of octol (2).