Supplementary Material (ESI) for Soft Matter

A pH Responsive Dendron-DNA-Protein Hybrid Supramolecular System

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1 General Information

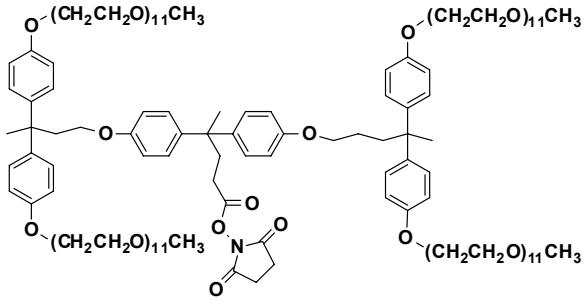
The oligonucleotides were purchased from TaKaRa Biotech (Dalian, China) and HPLC purified. Streptavidin (STV) was obtained from AMRESCO. All other chemicals were purchased from Sigma-Aldrich. All buffers were prepared with ultra-pure MilliQ water (resistance > 18 $M\Omega \cdot cm^{-1}$).

Unless otherwise noted, all synthetic experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 Spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz) or Bruker AMX-600 spectrometers (^{1}H: 600 MHz; ^{13}C: 150 MHz) at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) were denoted in Hz and chemical shifts (δ) in ppm. Multiplicities were denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Matrix-assisted laser desorption-ionization (time of flight) (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex III MOLDI-TOF spectrometer with α-cyano-4-hydroxylcinnamic acid (CCA) as the matrix. FAB spectra were carried out on a Bruker APEX 47E FTMS spectrometer. CD spectra were recorded on a JASCO-810 spectrometer. All the pH values mentioned were calibrated by a micro pH meter (FE 20 from METTLER TOLEDO company). UV/Vis spectra were recorded on a Varian Cary 100 spectrophotometer equipped with a programmable temperature-control unit.

Denaturing polyacrylamide gel electrophoresis (PAGE) (10% wt, Acr:Bis = 19:1, 3M Urea) was run at 20 V/cm in 1 × TBE buffer for 3 h. After the electrophoresis, the gel was stained with Stains-all dye (Sigma) or Coomassie Brilliant Blue R-250 (Fisher Biotech).

In a control experiment, the dendron G1 was synthesized, and reacted with 5'-NH_2-TTCCCTAACCCTAACCCTAACCCTT-biotin-3' to obtain DNA-G1 conjugate. Four DNA-G1 conjugates were assembled with streptavidin through noncovalent interaction to give G1-DNA-STV supramolecular system.

2 Preparation of the dendron (G1 and G2)-DNA conjugates.



G1

The dendron (G1 or G2) was dissolved in 75 mM pH 8.0 phosphate buffer solution and followed by adding 100 μM 5'-amino group of the biotinylated DNA with a stoichiometric molar ratio of dendron/DNA about 600:1. After incubating at room temperature for 6 h, the reaction mixture was analyzed and separated by denaturing PAGE. The resulting dendron-DNA conjugate cut off from the PAGE was dipped in water overnight, then the supernatant was desalted by ultrafiltration device (3k Da) or C18 reverse-phase column chromatograph. The final resulting product was freeze-dried to give the desired DNA-dendron conjugate. The concentration of re-dissolved conjugate was determined by measuring DNA absorbance at 260 nm using UV-Vis spectrophotometer.

3 Preparation of the dendron (G1 and G2)-DNA-STV conjugates

Conjugation of biotinylated DNA-dendron to streptavidin was carried out with a stoichiometric molar ratio of biotinylated DNA-dendrons/STV about 5:1 in pH 7.0 phosphate buffer at room temperature. After overnight incubation room temperature, the excess biotinylated DNA-dendrons and unreacted streptavidin were removed by denaturing PAGE. After desalting with a 10k Da MWCO ultrafiltration tube, the ultimate dendron-DNA-streptavidin conjugate could be obtained.

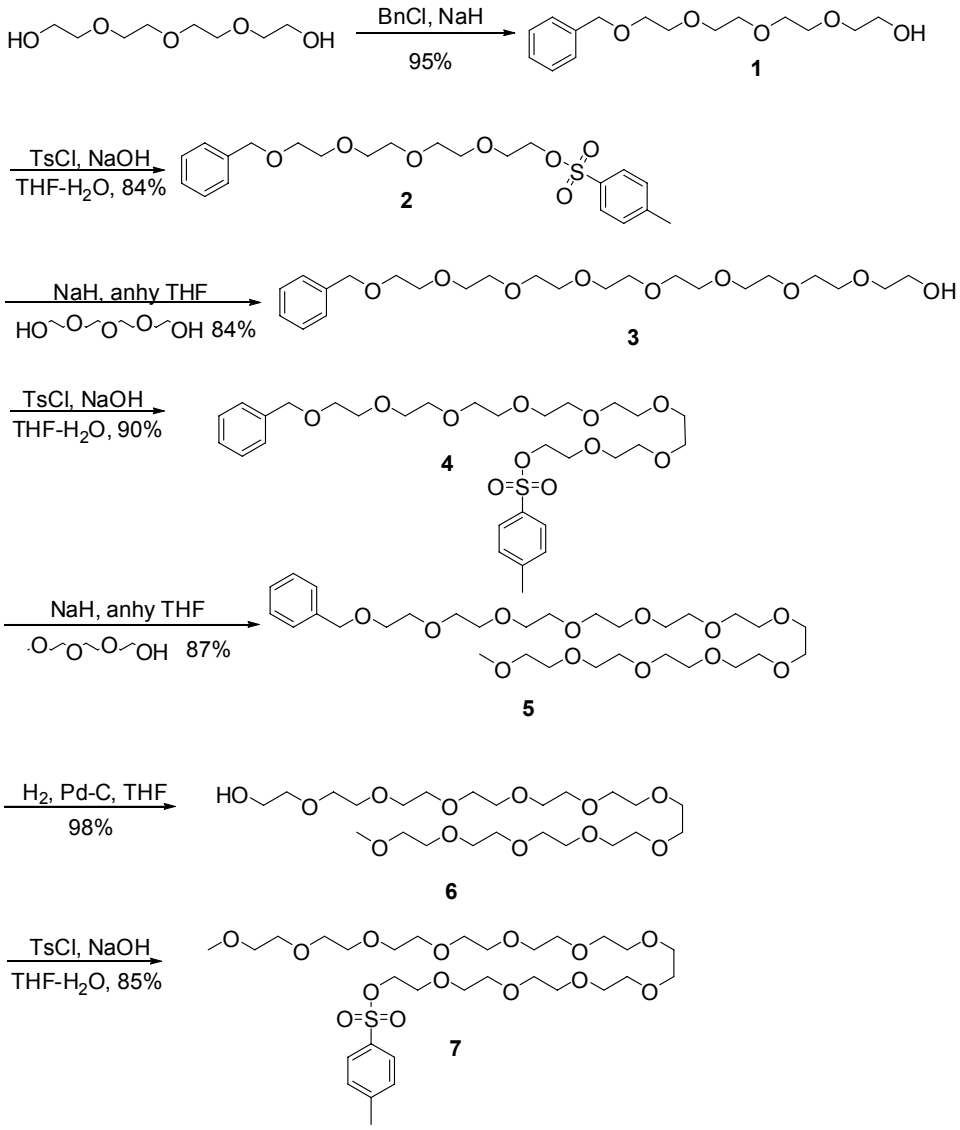
4 HABA test on the biotinylated DNA-dendron conjugates to STV

STV (AMRESCO) was dissolved in a mixture of 50 mM sodium phosphate (pH 5.0 and pH 6.2) and 150 mM NaCl at a concentration of 10 μM; and

2-(4-hydroxy-phenylazo)-benzoic acid (HABA) dye (Sigma) was dissolved the in 10 mM NaOH at a concentration of 10 mM. Then the streptavidin solution and HABA solution were mixed with a stoichiometric molar ratio about 1:50. The excess unbound HABA was removed by a 10k Da MWCO ultrafiltration tube. Subsequently, the prepared STV-HABA complex was titrated with the biotinylated DNA-dendron (G1 and G2) conjugate at different molar ratio (1:1 to 1:5) in pH 5.0 or pH 6.2 phosphate buffer monitored by UV-Vis spectroscopy.

5 Synthesis and characterization of amphiphilic dendrons

1) Synthesis of oligoethylene glycol derivatives (OEGs):



Scheme S1: Synthetic route to OEGs

Compound 1 [1]**:** To a three-necked flask, NaH (15.0 g, 70% in oil, 400 mmol) and THF (700 mL) were placed, and then, tetraethylene glycol (77.6 g, 400 mmol) was added slowly under ice bath. The mixture was heated to reflux, and THF solution (80 mL) of benzyl chloride (12.7 g, 100 mmol) was added dropwise. The reaction mixture was stirred for 3 hrs at 100 °C, and then, it was allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH, and 5 wt% aq. HCl (50 mL) was added. After evaporation of THF, the product was extracted using 5 wt% aq. HCl and CH_2Cl_2. The crude product (brownish liquid, 90% yield) obtained by solvent evaporation and drying under vacuum condition was used for the subsequent reaction without purification. The formation of bisbenzyl ether in ca. 10% molar ratio was observed in ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.47~3.59 (m, OC*H*$_2$C*H*$_2$O, 16H), 4.57 (s, ArC*H*$_2$O, 2H), 7.2~7.4 (m, Ar*H*, 5H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 138.8, 128.1, 127.5, 127.4, 72.9, 72.5, 70.4, 70.3, 70.1, 69.3, 61.3; ESI-MS calcd for $C_{15}H_{24}O_5$ 284.35, found 283.4(M-H$^+$)

Compound 2 [1]**:** Compound **1** (90% in purity, 25.0 g, 87 mmol), NaOH (14.00 g, 350 mmol), THF (80 mL), and H_2O (70 mL) were put to a three-necked flask, and the mixture was cooled at 0 °C. A THF solution (100 mL) of *p*-toluenesulfonyl chloride (19.2 g, 100 mmol) was added to the mixture dropwise, and the reaction mixture was stirred for 2 hrs at 0 °C. The reaction mixture was allowed to warm at room temperature, and stirred for additional 20 hrs. The reaction mixture was poured to 5wt% aq. HCl cooled at 0 °C, and the product was extracted with CH_2Cl_2. The organic layer was rinsed with water, and dried with Na_2SO_4. The crude product obtained by solvent evaporation was purified by column chromatography (5% to 10% THF/ CH_2Cl_2) afforded **2** (35.0 g, 80 mmol, 92%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.38 (s, C*H*$_3$Ar, 3H), 3.51~3.66 (m, OC*H*$_2$C*H*$_2$O, 14H), 4.09~4.12 (t, *J* = 9.45 Hz, ArOC*H*$_2$, 2H), 4.52 (s, ArC*H*$_2$O, 2H), 7.22~7.32 (m, Ar*H*, 7H), 7.74~7.77 (d, *J* = 8.2 Hz, Ar*H*, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 144.7, 138.3, 133.0, 129.8, 128.3, 127.9, 127.6, 127.5, 73.1, 70.6, 70.5, 70.4, 69.5, 69.4, 68.6, 21.5; MALDI-TOF MS calcd for $C_{22}H_{30}NaO_7S$ 461.52 (M+Na$^+$), found 460.8, $C_{22}H_{30}O_7KS$

477.63 ($M+K^+$), found 476.7.

Compound 3 [1]: Following the procedure for **1**. NaH (11.3 g, 70% in oil, 300 mmol), tetraethylene glycol (58.2 g, 300 mmol), **2** (32.8 g, 75 mmol), and THF (500 mL) yielded **3** as yellow oil (29.0 g, 63 mmol, 84%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.54~3.69 (m, OCH_2CH_2O, 32H), 4.54 (s, $ArCH_2O$, 2H), 7.23~7.34 (m, Ar*H*, 5H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 138.8, 128.1, 127.5, 127.4, 72.9, 72.5, 70.4, 70.3, 70.1, 69.3, 61.3; MALDI-TOF MS calcd for $C_{23}H_{40}NaO_9$ 483.55 ($M+Na^+$), found 482.9, $C_{23}H_{40}KO_9$ 499.66 ($M+K^+$), found 498.9

Compound 4 [1]: Following the procedure for **2, 3** (27.6 g, 60 mmol), NaOH (8.40 g, 210 mmol), *p*-toluenesulfonyl chloride (14.3 g, 75 mmol), and THF (50 mL), H_2O (50 mL) yielded **4** as yellow oil (33.2 g, 54.0 mmol, 90%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.41 (s, CH_3Ar, 3H), 3.53~3.67 (m, OCH_2CH_2O, 30H), 4.10~4.13 (t, *J* = 9.32 Hz, $ArOCH_2$, 2H), 4.53 (s, $ArCH_2O$, 2H), 7.22~7.32 (m, Ar*H*, 7H), 7.75~7.78 (d, *J* = 8.29 Hz, Ar*H*, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 144.7, 138.3, 132.9, 129.8, 128.2, 127.8, 127.6, 127.4, 73.0, 70.5, 70.4, 70.4, 70.4, 69.4, 69.3, 68.5, 21.5; MALDI-TOF MS calcd for $C_{30}H_{46}NaO_{11}S$ 637.73 ($M+Na^+$), found 637.0, $C_{30}H_{46}O_{11}$ KS 653.84 ($M+K^+$), found 653.0

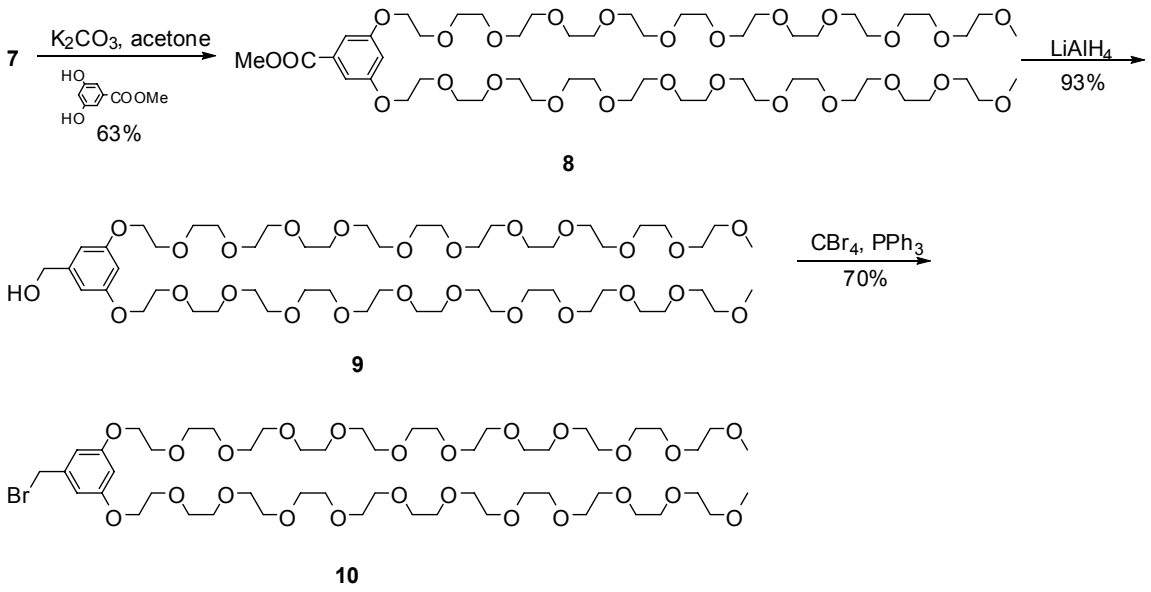
Compound 5: Following the procedure for **1** NaH (1.7 g, 50 mmol, 70% in oil), triethylene glycol monomethyl ether (8.2 g, 50 mmol), **4** (30.7 g, 50 mmol), and THF (300 mL) yielded **5** as yellow oil (26.4 g, 43.5 mmol, 87%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.36 (s, CH_3OCH_2, 3H), 3.50~3.63 (m, OCH_2CH_2O, 44H), 4.54 (s, $ArCH_2O$, 2H), 7.29~7.33 (m, Ar*H*, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 138.3, 128.2, 127.6, 127.4, 73.1, 71.8, 70.5, 70.4, 69.4, 58.8; MALDI-TOF MS calcd for $C_{30}H_{54}NaO_{12}$ 629.73 ($M+Na^+$), found 629.5, $C_{23}H_{40}KO_9$ ($M+K^+$) 645.84, found 645.5

Compound 6: To an autoclave, **5** (3.10 g, 5 mmol), palladium carbon (5wt%, 200 mg), and THF (5 mL) were put, and the autoclave was sealed. H_2 gas (50 atm) was

introduced to the autoclave, and the reaction mixture was stirred for 12 hrs at 80 °C. The autoclave was allowed to cool at room temperature and depressurized to open. The product was obtained by filtration off palladium carbon and solvent evaporation in 98% yield as colorless solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.37 (s, C*H*$_3$OCH$_2$, 3H), 3.38~3.73 (m, OC*H*$_2$C*H*$_2$O, 44H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 72.5, 71.8, 70.5, 70.4, 70.3, 61.6, 58.9; MALDI-TOF MS calcd for $C_{23}H_{48}NaO_{12}$ 539.61 ($M+Na^+$), found 539.4, $C_{23}H_{48}KO_{12}$ ($M+K^+$) 555.72, found 555.4

Compound 7: Following the procedure for **2**. **6** (20.6 g, 40 mmol), NaOH (5.60 g, 140 mmol), *p*-toluenesulfonyl chloride (9.6 g, 50 mmol), and THF (50 mL), H_2O (50 mL) yielded **7** as yellow oil (22.8 g, 34 mmol, 85%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, C*H*$_3$Ar, 3H), 3.36 (s, C*H*$_3$OCH$_2$, 3H), 3.36~3.68 (m, OC*H*$_2$C*H*$_2$O, 42H), 4.12~4.15 (t, *J* = 9.28 Hz, ArOC*H*$_2$, 2H), 7.33~7.36 (d, *J* = 8.13 Hz, Ar*H*, 2H), 7.77~7.79 (d, *J* = 8.28 Hz, Ar*H*, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 144.7, 138.3, 133.0, 129.8, 128.3, 127.9, 127.6, 127.5, 73.1, 70.6, 70.5, 70.4, 69.5, 69.4, 68.6, 21.5; MALDI-TOF MS calcd for $C_{30}H_{54}O_{14}NaS$ 693.8 ($M+Na^+$), found 693.5, $C_{30}H_{54}O_{14}KS$ 709.9($M+K^+$), found 709.5

2) Synthesis of peripheral OEG-modified Dendrons:



Scheme S2. Synthetic route to OEG Dendron

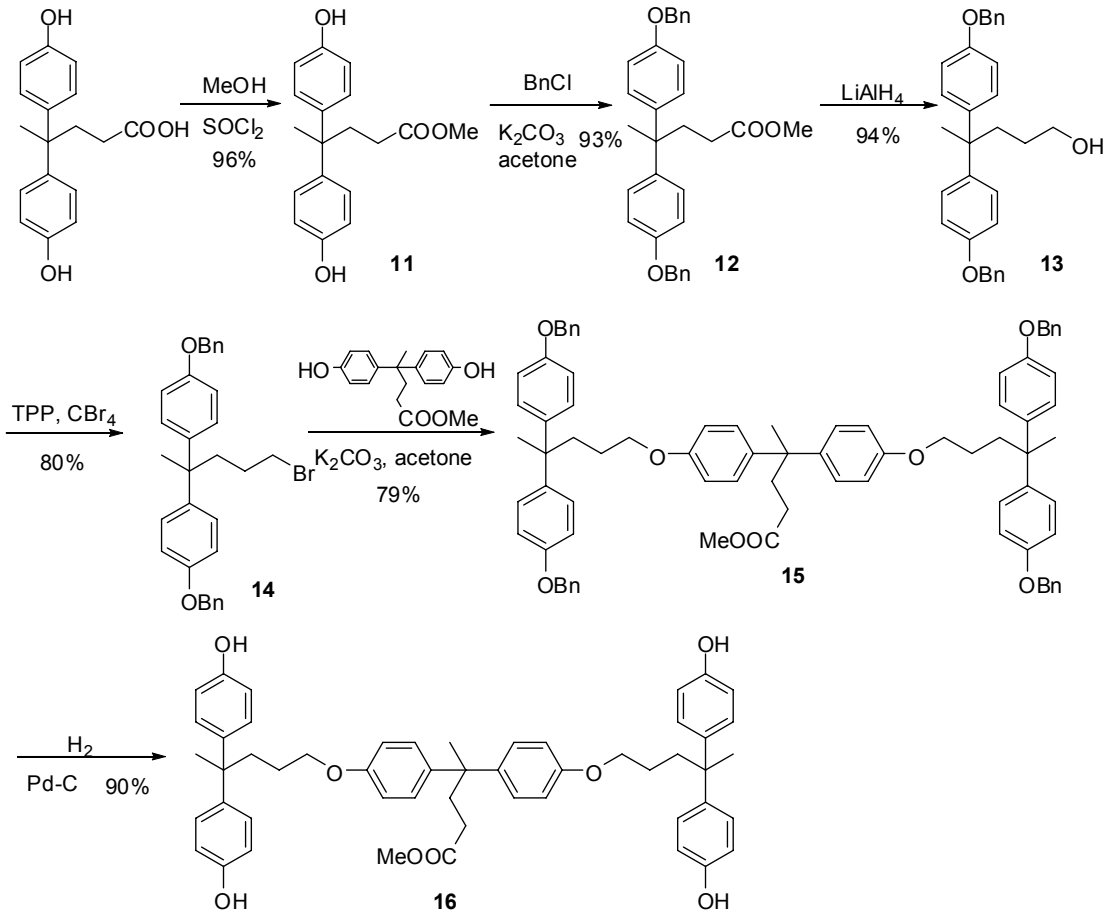
Compound 8: A mixture of 3, 5-dihydrobenzoate (2.35 g, 14 mmol), **7** (20.1 g, 30 mmol), and K_2CO_3 (13.8 g, 100 mmol) in acetone was stirred at reflux for 16 h. The product was diluted with CH_2Cl_2, filtered, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (150 ml), washed with water (100 ml) and then dried over Na_2SO_4. The crude product obtained by solvent evaporation was purification by column chromatography (2% to 8% MeOH/CH_2Cl_2) afforded Compound **8** as a yellow oil (10.2 g, 8.7 mmol, 63%). ^{1}H NMR($CDCl_3$, 300 MHz): δ = 3.36 (s, CH_2OCH_3, 6H), 3.51~3.71 (m, OCH_2CH_2O and $COOCH_3$, 83H), 3.84-3.87 (m, $ArOCH_2CH_2O$, 4H), 4.12~4.14 (m, $ArOCH_2CH_2O$,, 4H), 6.69 (s, Ar*H*, 1H), 7.21~7.22 (d, *J* = 1.88 Hz, Ar*H*, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.2, 159.6, 131.8, 108.2, 106.9, 71.8, 70.7, 70.5, 70.4, 70.3, 69.5, 67.6, 58.9; MALDI-TOF MS calcd for $C_{54}H_{100}NaO_{26}$ ($M+Na^+$) 1188.35, found 1187.8, $C_{54}H_{100}O_{26}K$ ($M+K^+$)1204.45, found 1203.8

Compound 9: $LiAlH_4$ (0.42 g, 11 mmol) was added to a solution of Compound **8** (10.0 g, 8.6 mmol) in dry THF (100 mL) at 0 °C, the mixture was stirred for 10 min, warmed to room temp, and then reflux for another 45 min. The reaction was quenched by dropwise addition of saturated NH_4Cl solution. The resulting precipitate was filtered, and THF was evaporated. The residue was purification by column chromatography with (10% MeOH/CH_2Cl_2) afforded **9** (9.09 g, 8.0 mmol, 93%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.30 (s, $ArCH_2OH$, 1H), 3.36 (s, CH_3OCH_2, 6H), 3.53~3.70 (m, OCH_2CH_2O, 80H), 3.80~3.83 (m, OCH_2CH_2O, 4H), 4.07~4.19 (m, $ArOCH_2$, 4H), 4.56 (s, $ArCH_2OH$, 2H), 6.37 (s, Ar*H*, 1H), 6.51~6.52 (d, *J* = 1.67 Hz, Ar*H*, 2H); ^{13}C NMR ($CDCl_3$, 75MHz): δ = 159.9, 144.0, 105.3, 100.6, 71.8, 70.7, 70.4, 70.3, 69.6, 67.4, 64.4, 58.8; MALDI-TOF MS calcd for $C_{53}H_{100}NaO_{25}$ 1160.34 ($M+Na^+$), found 1159.8, $C_{53}H_{100}O_{25}K$ 1176.44 ($M+K^+$), found 1175.8

Compound 10: To an ice-cooled solution of Compound **9** (8.9 g, 7.8 mmol) and CBr_4 (4.16 g, 12.5 mmol) in dry THF (15 ml) was added a solution of PPh_3 (2.88 g, 11 mmol) in dry THF (5 ml) dropwise over 10 minutes. The resulting mixture was stirred

in ice for 10 minutes and at room temperature for 10 minutes. The solvent was removed under reduced pressure and the product was purified by column chromatography (15% to 50% THF/CH_2Cl_2) afford **10** (6.55 g, 5.46 mmol, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.37 (s, C*H*$_3$OCH$_2$, 6H), 3.53~3.70 (m, OC*H*$_2$C*H*$_2$O, 80H), 3.80~3.83 (t, *J* = 9.46 Hz, OC*H*$_2$C*H*$_2$O, 4H), 4.07~4.10 (t, *J* = 9.51 Hz, ArOC*H*$_2$, 4H), 4.39 (s, ArC*H*$_2$Br, 2H), 6.41 (s, Ar*H*, 1H), 6.54~6.55 (d, *J* = 1.15 Hz, Ar*H*, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.9, 139.5, 107.7, 101.6, 71.8, 70.7, 70.5, 70.4, 70.3, 69.5, 67.4, 58.9, 33.5; MALDI-TOF MS calcd for $C_{53}H_{99}BrNaO_{25}$ 1223.23 ($M+Na^+$), found 1223.7, $C_{53}H_{100}O_{25}BrK$ 1239.34 ($M+K^+$), found 1239.7

3) Synthesis of hydrophobic core:



Scheme S3. Synthetic route to Hydrophobic Core

Compound 11: $SOCl_2$ (11.9 g, 100 mmol) was added dropwise to the solution of 4,4-bis (4-hydroxyphenyl) valeric acid (14.3 g, 50 mmol) in MeOH (120 ml) at

ambient temperature, the mixture was stirred for another 30 minutes. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2, white solid was obtained (14.4 g, 48 mmol, 96%). ^{1}H NMR (^{6}d-Acetone, 300 MHz): δ = 1.54 (s, C*H*$_3$, 3H), 2.05~2.12 (m, C*H*$_2$, 2H), 2.34~2.39 (m, C*H*$_2$, 2H), 3.56 (s, COOC*H*$_3$, 3H), 6.75~6.78 (d, *J* = 8.71 Hz, Ar*H*, 4H), 7.02~7.05 (d, *J* = 8.74 Hz, Ar*H*, 4H); ^{13}C NMR (^{6}d-Acetone, 75 MHz): δ = 207.5, 174.8, 156.1, 156.0, 140.9, 129.0, 115.6, 115.5, 51.7, 45.0, 37.6, 30.7, 28.1; ESI-MS calcd for $C_{18}H_{20}O_4$: 300.35, found 299.17(M-H$^+$)

Compound 12: Following the procedure for **8, 11** (13.5 g, 45 mmol), BnCl (12.7 g, 100 mmol), and K_2CO_3 (27.6 g, 200 mmol) in acetone yielded **12** as a colorless solid (20.16 g, 42 mmol, 93%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.56 (s, C*H*$_3$, 3H), 2.07~2.13 (m, C*H*$_2$, 2H), 2.37~2.43 (m, C*H*$_2$, 2H), 3.59 (s, COOC*H*$_3$, 3H), 5.00 (s, ArOC*H*$_2$, 4H), 6.85~6.88 (d, *J* = 8.82 Hz, Ar*H*, 4H), 7.08~7.11 (d, *J* = 8.78 Hz, Ar*H*, 4H), 7.27~7.42 (m, Ar*H*, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 174.4, 156.9, 141.3, 137.2, 128.6, 128.3, 128.0, 127.6, 114.3, 70.0, 51.6, 44.6, 36.7, 30.2, 27.8; MALDI-TOF MS calcd for $C_{32}H_{32}NaO_4$ 503.58 (M+Na$^+$), found, 502.8; $C_{32}H_{32}K\,O_4$ 519.69 (M+K$^+$), found 518.8

Compound 13[2]**:** Following the procedure for **9**. $LiAlH_4$ (1.9 g, 50 mmol) in THF (15 mL) and **13** (19.2 g, 40 mmol) in THF (100 mL) yielded **12** (17.0 g, 37.6 mmol, 94%) as viscous liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.52~1.57 (t, *J* = 14.4 Hz, C*H*$_2$, 2H), 1.80 (s, C*H*$_3$, 3H), 2.26~2.32 (m, C*H*$_2$, 2H), 2.63 (s, CH_2O*H*, 1H), 3.67~3.71 (m, C*H*$_2$, 2H), 5.16 (s, ArOC*H*$_2$, 4H), 7.08~7.10 (d, *J* = 8.75 Hz, Ar*H*, 4H), 7.32~7.35 (d, *J* = 9.0 Hz, Ar*H*, 4H), 7.47~7.62 (m, Ar*H*, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.9, 142.4, 137.4, 128.8, 128.6, 128.1, 127.8, 114.5, 77.7, 70.1, 63.3, 44.9, 38.3, 28.4, 28.2; MALDI-TOF MS calcd for $C_{31}H_{32}NaO_3$ (M+Na$^+$) 475.57, found, 474.8

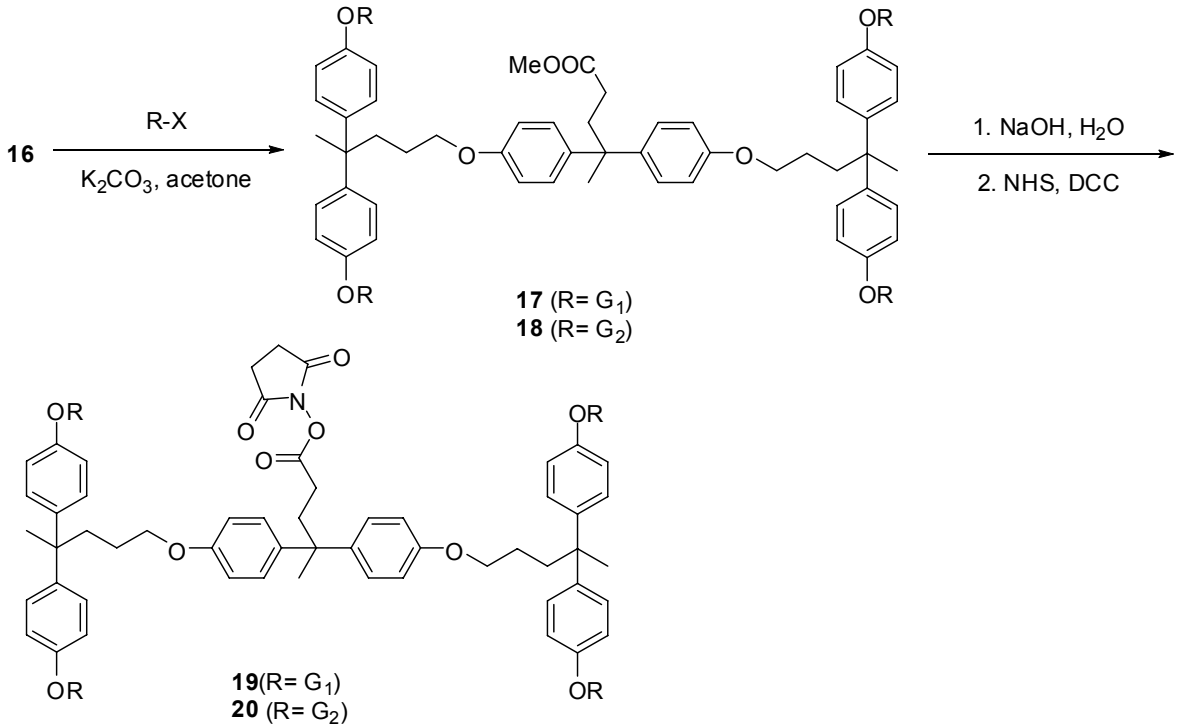
Compound 14[2]**:** Following the procedure for **10**. **13** (16.0 g, 35.4 mmol), PPh_3 (16.0 g, 35.4 mmol), CBr_4 (14.1 g, 42.5 mmol), and dry THF (30 mL) yielded **14** as yellow oil (14.6 g, 28.3 mmol, 80%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.81~1.87 (m, C*H*$_3$+C*H*$_2$, 5H), 2.37~2.42 (m, C*H*$_2$, 2H),

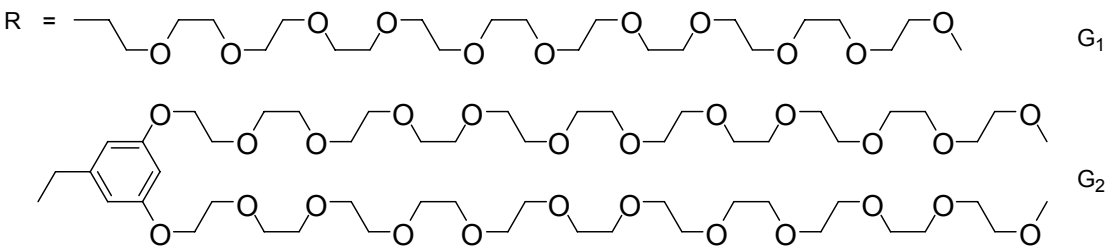
3.49~3.53 (t, *J* = 12.6, C*H*$_2$, 2H), 5.20(s, ArOC*H*$_2$, 4H), 7.10~7.13 (d, *J* = 8.49 Hz, Ar*H*, 4H), 7.32~7.35 (d, *J* = 8.50 Hz, Ar*H*, 4H), 7.48~7.64 (m, Ar*H*, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 157.0, 141.9, 137.4, 128.8, 128.5, 128.2, 127.8, 114.5, 77.7, 70.2, 44.9, 40.9, 34.9, 28.7, 28.4; ESI-MS calcd for $C_{31}H_{31}BrO_2$ 515.48, found, 517.3

Compound 15: Following the procedure for **8**. **14** (10.3 g, 20 mmol), **11** (2.7 g, 9 mmol), and K_2CO_3 (6.9 g, 50 mmol) in acetone yielded **15** as a colorless solid (8.30 g, 7.1 mmol, 79%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.53~1.61 (m, C*H*$_3$+C*H*$_2$, 13H), 2.04~2.08 (m, C*H*$_2$, 2H), 2.11~2.21 (m, C*H*$_2$, 4H), 2.35~2.41 (t, *J* = 16.4, C*H*$_2$, 2H), 3.60 (s, COOC*H*$_3$, 3H), 3.82~3.86 (t, *J* = 11.26 Hz, C*H*$_2$O, 4H), 5.02 (s, ArOC*H*$_2$, 8H), 6.72~6.75 (d, *J* = 8.76 Hz, Ar*H*, 4H), 6.85~6.88 (d, *J* = 8.80 Hz, Ar*H*, 4H), 7.04~7.07 (d, *J* = 8.77 Hz, Ar*H*, 4H), 7.10~7.13 (d, *J* = 8.78 Hz, Ar*H*, 4H), 7.30~7.43 (m, Ar*H*, 20H); ^{13}C NMR ($CDCl_3$, 75M Hz): δ = 174.38, 157.1, 156.7, 142.0, 140.9, 137.2, 128.5, 128.3, 128.2, 127.9, 127.5, 126.7, 114.2, 113.9, 70.0, 68.3, 51.5, 44.8, 44.5, 38.4, 36.7, 30.1, 27.9, 27.7, 25.0; MALDI-TOF MS calcd for $C_{31}H_{32}NaO_3$ 1192.48 (M+Na$^+$), found, 1191.5

Compound 16: Following the procedure for **6**. **15** (8.0 g, 6.84 mmol), palladium carbon (5wt%, 500 mg) in THF yielded **16** as a colorless solid (5.0 g, 6.18 mmol, 90%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.54~1.57 (m, C*H*$_3$+C*H*$_2$, 13H), 2.04~2.08 (m, C*H*$_2$, 2H), 2.16~2.21 (m, C*H*$_2$, 4H), 2.33~2.39 (t, *J* = 16.6 Hz, C*H*$_2$, 2H), 3.55 (s, COOC*H*$_3$, 3H), 3.68 (s, ArO*H*, 4H), 3.86~3.90 (t, *J* = 12.2 Hz, C*H*$_2$O, 4H), 5.02 (s, ArOC*H*$_2$, 8H), 6.72~6.75 (d, *J* = 8.76 Hz, 4H), 7.04~7.09 (m, Ar*H*, 12H), 6.75~6.79 (m, Ar*H*, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 207.5, 174.8, 158.1, 155.9, 155.8, 141.8, 141.6, 129.1, 129.0, 115.6, 115.5, 114.9, 69.1, 51.8, 45.3, 45.2, 39.1, 37.5, 28.5, 28.1, 25.9; MALDI-TOF MS calcd for $C_{52}H_{56}NaO_8$ 831.99 (M+Na$^+$), found, 831.6

4) Synthesis of hydrophilic dendrons:





Scheme S4. Synthetic route to Hydrophilic Dendron

Compound 17: Following the procedure for **8**. **7** (1.71 g, 2.6 mmol), **16** (0.47 g, 0.58 mmol), and K_2CO_3 (1.38 g, 10 mmol) in acetone yielded **17** as a colorless oil (1.08 g, 0.38 mmol, 66%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.51~1.56 (m, C*H*$_3$+C*H*$_2$, 13H), 2.05~2.06 (m, C*H*$_2$, 2H), 2.14~2.16 (m, C*H*$_2$, 4H), 2.34~2.35 (m, C*H*$_2$, 2H), 3.34(d, *J* = 1.14 Hz, C*H*$_3$OCH$_2$, 12H), 3.50~3.67 (m, OC*H*$_2$C*H*$_2$O+COOC*H*$_3$, 163H), 3.79~3.80 (m, C*H*$_2$OAr, 12H), 4.04~4.05 (m, C*H*$_2$OAr, 8H), 6.70~6.71 (d, *J* = 8.52 Hz, Ar*H*, 4H), 6.75~6.77 (d, *J* = 8.58, Ar*H*, 8H), 7.01~7.03 (d, *J* = 8.46 Hz, Ar*H*, 4H), 7.05~7.06 (d, *J* = 8.52 Hz, Ar*H*, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 174.4, 157.1, 156.7, 141.9, 140.9, 128.3, 128.19, 113.9, 113.9, 71.9, 71.5, 70.8, 70.6, 70.6, 69.8, 68.3, 67.3, 59.1, 51.6, 44.8,

44.5, 38.4, 36.7, 30.2, 28.0, 27.9, 25.0; MALDI-TOF calcd for $C_{144}H_{240}NaO_{52}$ 2826.4 ($M+Na^+$), found 2825.7, $C_{144}H_{240}KO_{52}$ 2842.5 ($M+K^+$), found 2841.7

Compound 18: Following the procedure for **8, 10** (2.2 g, 1.83 mmol), **16** (0.24 g, 0.3 mmol), and K_2CO_3 (1.38 g, 10 mmol) in acetone yielded **21** as a colorless oil (1.41 g, 0.27 mmol, 89%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.53~1.60 (m, C*H*$_3$+C*H*$_2$, 13H), 2.05~2.08 (m, C*H*$_2$, 2H), 2.16~2.17 (m, C*H*$_2$, 4H), 2.37~2.38 (m, C*H*$_2$, 2H), 3.36 (s, C*H*$_3$OCH$_2$, 24H), 3.52~3.71 (m, OC*H*$_2$C*H*$_2$O+COOC*H*$_3$, 323H), 3.81~3.83 (m, C*H*$_2$OAr, 20H), 4.08~4.09 (m, OC*H*$_2$C*H*$_2$O, 16H), 4.92 (s, ArC*H*$_2$OAr, 8H), 6.42 (s, Ar*H*, 4H), 6.57~6.58 (d, *J* = 1.62 Hz, Ar*H*, 8H), 6.73~6.75 (d, *J* = 8.7 Hz, Ar*H*, 4H), 6.84~6.85 (d, *J* = 8.7 Hz, Ar*H*, 8H), 7.05~7.06 (d, *J* = 8.64 Hz, Ar*H*, 4H), 7.09~7.11 (d, *J* = 8.7 Hz, Ar*H*, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 174.3, 160.1, 157.0, 156.6, 142.0, 140.8, 139.6, 128.3, 128.2, 114.2, 113.9, 106.0, 101.0, 71.9, 71.5, 70.8, 70.6, 70.5, 69.9, 69.7, 68.3, 67.5, 59.0, 53.7, 51.5, 44.8, 44.5, 38.4, 36.7, 30.1, 28.0, 27.9, 25.0; MALDI-TOF calcd for $C_{264}H_{448}NaO_{104}$ 5309.31 ($M+Na^+$), found 5312.6, $C_{264}H_{448}KO_{104}$ 5325.42 ($M+K^+$), found 5328.6

Compound 19: 1.62 g (0.58 mmol) **20** and 200 mg NaOH (5 mmol) was dissolved in 10 ml H_2O, the solution was stirred at reflux for 24h, 1 ml HCl (6 mol/L) was added, the product was extract with CH_2Cl_2. The organic layer was dried with Na_2SO_4, the crude product obtained by solvent evaporation was used without further purification. 1.0 g (0.36 mmol) acid and 76 mg HOSu (0.66 mmol) was dissolved in CH_2Cl_2 (5 ml), 168 mg DCC (0.82 mmol) was added to the solution. The solution was stirred for 24 h. The crude product obtained by solvent evaporation was purified by column chromatography (3% to 5% MeOH/CH_2Cl_2) afforded **19** (0.66 g, 0.23 mmol, 64%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.55~1.59 (m, C*H*$_3$+C*H*$_2$, 13H), 2.16~2.19 (m, C*H*$_2$, 4H), 2.31~2.33 (m, C*H*$_2$, 2H), 2.35~2.36 (m, C*H*$_2$, 2H), 2.88 (s, O=C-C*H*$_2$C*H*$_2$-C=O, 4H), 3.37 (s, C*H*$_3$OCH$_2$, 12H), 3.53~3.71 (m, OC*H*$_2$C*H*$_2$O, 160H), 3.83~4.07 (m, OC*H*$_2$C*H*$_2$O, 12H), 4.06~4.08 (m, C*H*$_2$OAr, 8H), 6.74~6.76 (d, *J* =8.52 Hz, Ar*H*, 4H), 6.78~6.80 (d, *J* =8.58 Hz, Ar*H*, 8H), 7.04~7.06 (d, *J* = 8.46 Hz,

Ar*H*, 4H), 7.08~7.09 (d, *J* = 8.52 Hz, Ar*H*, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 69.4, 169.0, 157.2, 156.6, 141.9, 140.2, 128.2, 128.1, 114.1, 113.9, 71.9, 71.5, 70.8, 70.6, 70.6, 70.5, 70.4, 69.8, 68.3, 67.3, 61.6, 59.0, 53.7, 44.8, 44.5, 38.4, 36.3, 28.0, 27.8, 27.3, 25.6, 25.0; MALDI-TOF calcd for $C_{147}H_{241}NNaO_{54}$ 2909.45 ($M+Na^+$), found2914.3, $C_{147}H_{241}NKO_{54}$ 2925.56 ($M+K^+$), found 2930.5

Compound 20: Following the procedure for 19, 1.41 g (0.27 mmol) 18 was hydrolysised and reacted with 45 mg HOSu (0.39 mmol) and 100 mg DCC (0.48 mmol), colorless oil (0.7 g, 0.13 mmol, 60%) after purification by flash column chromatography. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.54~1.61 (m, C*H*$_3$+C*H*$_2$, 13H), 2.18~2.19 (m, C*H*$_2$, 4H), 2.34~2.36 (m, C*H*$_2$, 2H), 2.59~2.61 (m, C*H*$_2$, 2H), 2.82 (s, O=C-C*H*$_2$C*H*$_2$-C=O, 4H), 3.37 (s, CH3OCH2, 24H), 3.53~3.71 (m, OC*H*$_2$C*H*$_2$O, 320H), 3.82~3.84 (m, OC*H*$_2$C*H*$_2$O, 20H), 4.09~4.10 (m, OC*H*$_2$C*H*$_2$O, 16H), 4.93 (s, ArC*H*$_2$O, 8H), 6.43 (s, Ar*H*, 4H), 6.58~6.59 (d, J = 1.62 Hz, Ar*H*, 8H), 6.76~6.77 (d, J = 8.52 Hz, Ar*H*, 4H), 6.84~6.86 (d, J = 8.52 Hz, Ar*H*, 8H), 7.06~7.07 (d, J = 8.58 Hz, Ar*H*, 4H), 7.11~7.12 (d, J = 8.52 Hz, Ar*H*, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 171.9, 171.4, 169.4, 168.9, 161.0, 160.4, 160.0, 159.9, 157.1, 156.6, 141.9, 140.2, 139.5, 128.2, 128.0, 114.2, 114.0, 113.9, 105.9, 100.9, 71.9, 71.5, 71.2, 70.7, 70.6, 70.5, 70.4, 69.7, 69.6, 68.8, 68.4, 67.5, 62.9, 58.9, 53.8, 44.8, 44.5, 38.3, 27.9, 27.8, 25.5, 25.3, 24.9; MALDI-TOF calcd for C267H449KNO106 5408.46 (M+K+), found 5438.

6 MALDI-TOF of dendron(G1 and G2)-DNA conjugates

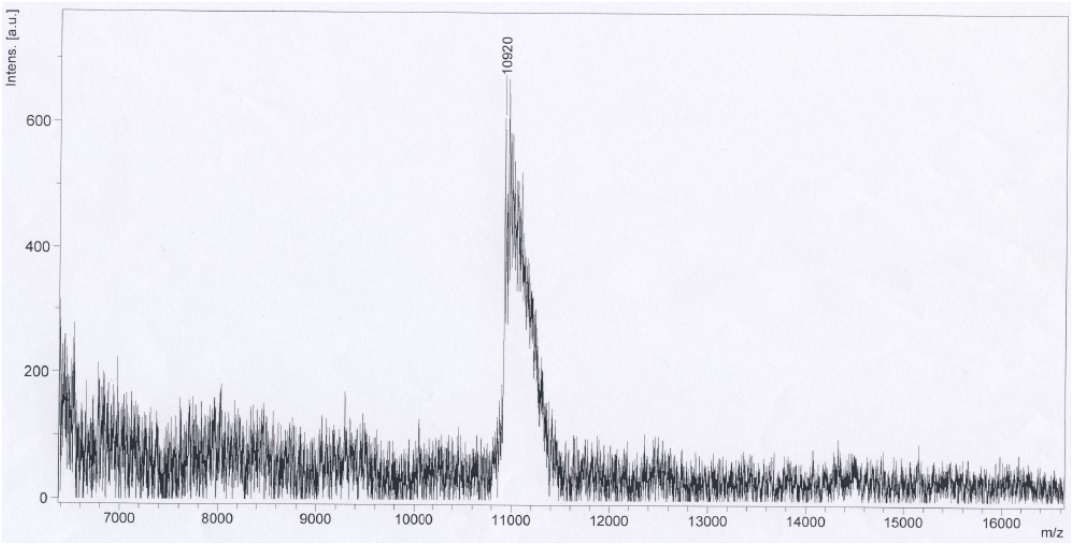


Fig.S1 MALDI-TOF corresponding to dendrion G1-DNA conjugate (calculated *m/z* $[M+H]^+$ =10772).

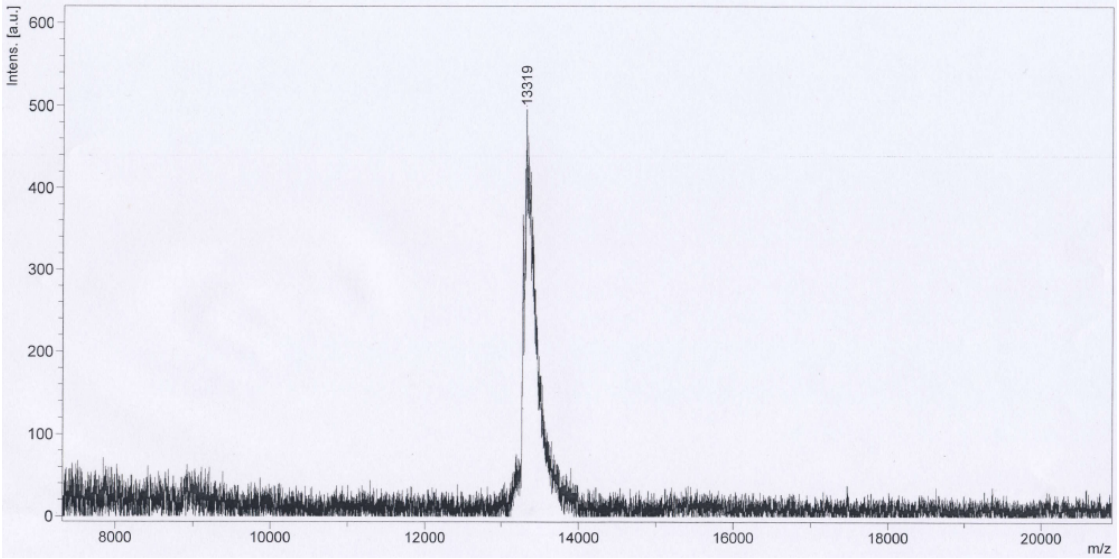


Fig.S2 MALDI-TOF corresponding to dendron G2-DNA conjugate (calculated *m/z* $[M+H]^+$ =13208).

7 Characterization of G1-DNA-STV conjugate by PAGE

The prepared biotinylated DNA-G1 conjugate was assembled with STV in a pH 7.0 phosphate buffer at room temperature for 12 hours at different molar ratio (1:1 up to 10:1), and the results were analyzed by denature PAGE (10% wt, Acr : Bis = 19:1, 3M Urea). As shown in **Fig. S3**, when the ratios lower than 4:1 were employed, several bands were observed. Along with the increase of DNA-G1 ratio in the assembling system, the yield of assemblies containing more DNA-G1 increased. When the ratio reached 4:1, only one obvious band was observed in the assembly area. No new product band was observed when we increased the ratio to 10:1.

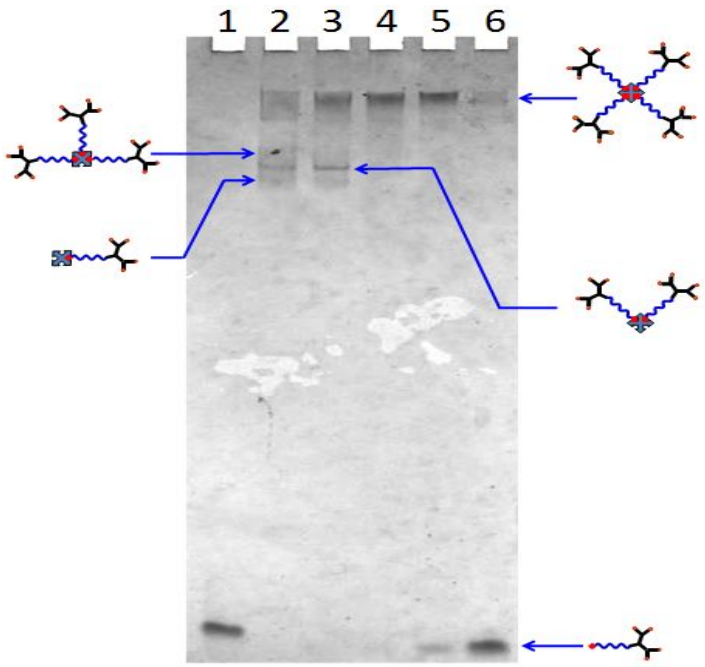


Fig.S3 Characterization of STV and G1-DNA conjugate assembly by PAGE.
Lane1, G1-DNA conjugate; Lane2, STV:G1-DNA=1:1; Lane3, STV:G1-DNA=1:3; Lane4, STV:G1-DNA=1:3; Lane5, STV:G1-DNA=1:4; Lane6, STV:G1-DNA=1:10.

8 Identification of the STV-DNA-dendron conjugates after gel purification

The identification of the ultimate STV-DNA-dendron conjugates after gel purification was shown in the **Fig. S4**. It is well-known that Stains-All is used for staining of nucleic acids, and Coomssie Brilliant Dyes are a family of dyes commonly used to stain proteins. As shown in **Fig. S4**, lane 4, 5 and lane 8, 9, the purified (dendron-DNA)$_4$-STV conjugates which consist of nucleic acid and protein could be stained by both of the dyes to give one obvious band, respectively. While the DNA and dendron-DNA conjugates which only contain nucleic acids could be stained by Stains-All (**Fig. S4**, lane 1, 2, 3), but could not be stained by Coomssie Brilliant Blue (**Fig. S4**, lane 10, 11, 12). Similarly, the protein STV could only be stained by Coomssie Brilliant Blue (**Fig. S4**, lane 7), and no band could be found in the case of employing Stains-All (**Fig. S4**, lane 6). These results suggest that our hybrid supramolecular system are indeed comprised of both DNA and protein.

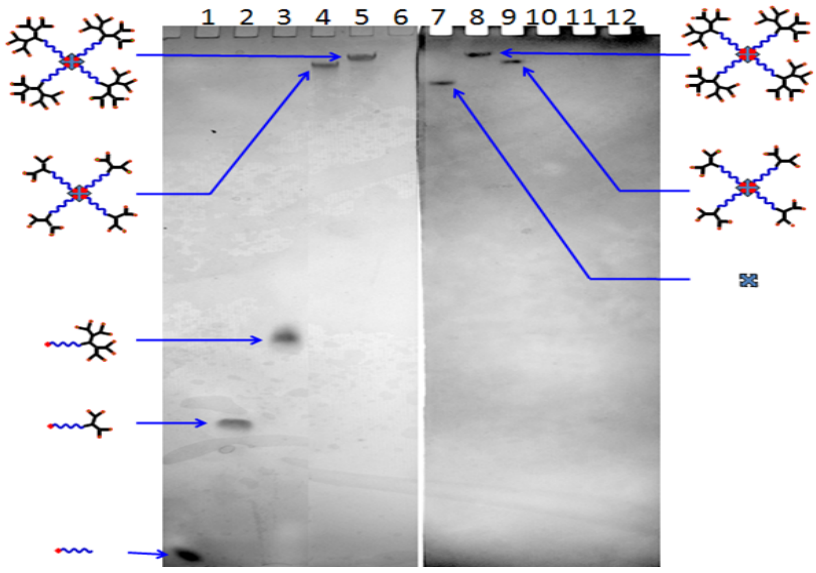


Fig. S4 Identification of the STV-DNA-dendrions conjugates after gel purification; Lane 1-6 panels of the gel are stained with Stained All for the oligonucleotide, and Lane 7-12 panels of the gel are stained with Coomssie Brilliant Blue for the STV; Lane 1, the DNA M; Lane 2, G1-DNA; Lane 3, G2-DNA; Lane 4, STV-(DNA-G1)$_4$; Lane 5, STV-(DNA-G2)$_4$; Lane 6, STV; Lane 7, STV; Lane 8, STV-(DNA-G2)$_4$; Lane 9, STV-(DNA-G1)$_4$; Lane 10, G2-DNA; Lane 11, G1-DNA; Lane 12, the DNA M.

9 UV-Vis absorption spectra of the dendrons (G1 andG2) and Gn-DNA conjugates

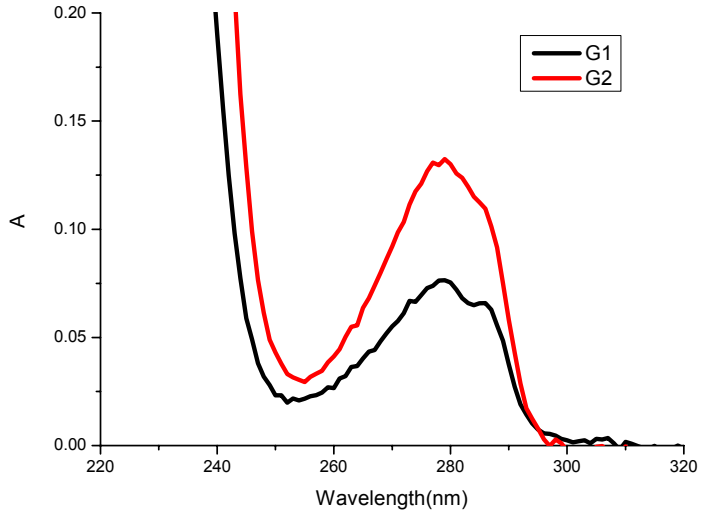


Fig. S5 UV-Vis absorption spectra of the dendron G1 (black) and G2 (red)

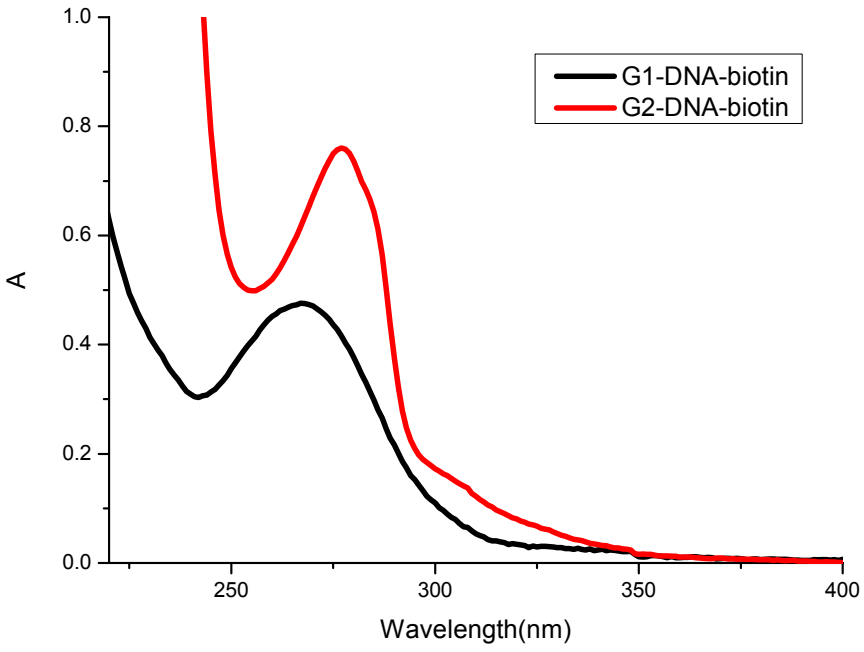


Fig. S6 UV-Vis absorption spectra of the conjugate dendron G1-DNA (black) and G2-DNA (red).

10 Spectral results from the titration of HABA-STV complex with biotinylated Gn-DNA

With the HABA–STV complex in hand, we titrated it with biotinylated DNA-G1 at pH 6.2. Upon the addition of DNA-G1, an immediate decrease in the absorption at 500 nm was detected, indicative of the displacement of HABA from STV, and an increase in the absorption at 350 nm was observed which was caused by the released HABA from the HABA-STV complex (**Fig**. **S7**). Since the dendron G2 and G2-DNA conjugate have a larger absorption at around 300 nm (**Fig. S5** and **S6**), the peak value at 350 nm during the titration by biotinylated DNA-G2 was less clear (**Fig. 4** in the manuscript). The titration required exactly four molar equivalents of DNA-G1 to STV, after which no further decrease in HABA absorbance at 500 nm was detected. These results demonstrated that the biotin unit in DNA-G1 conjugate has greater affinity to STV than HABA with the stoichiometry of 4:1. In order to examine whether the formation of i-motif could inhibit binding of the biotinylated DNA-dendron conjugates to STV, we carried out the same experiments at pH 5.0. As can be seen in **Fig. S8** and **Fig. S9**, STV could still bind DNA-G1 and DNA-G2 conjugates tightly, indicating that the steric i-motif did not hamper the formation of biotin-STV complex.

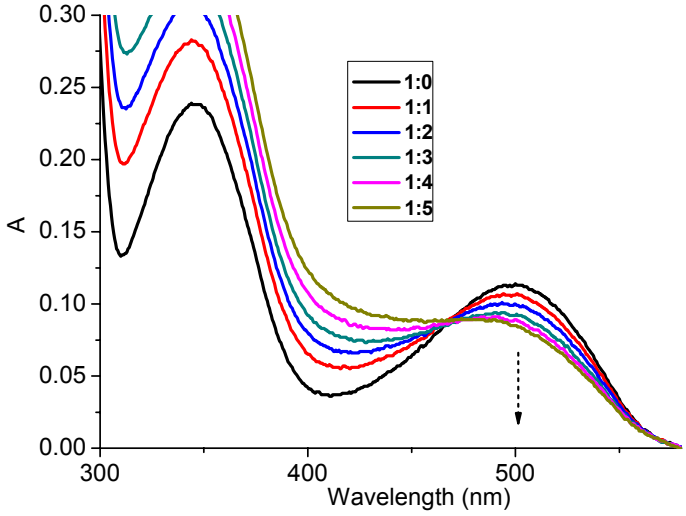


Fig. S7 Spectral results from the titration of HABA-STV complex with biotinylated DNA-G1 at pH 6.2 resulting in HABA release and a corresponding decrease in A_{500}.

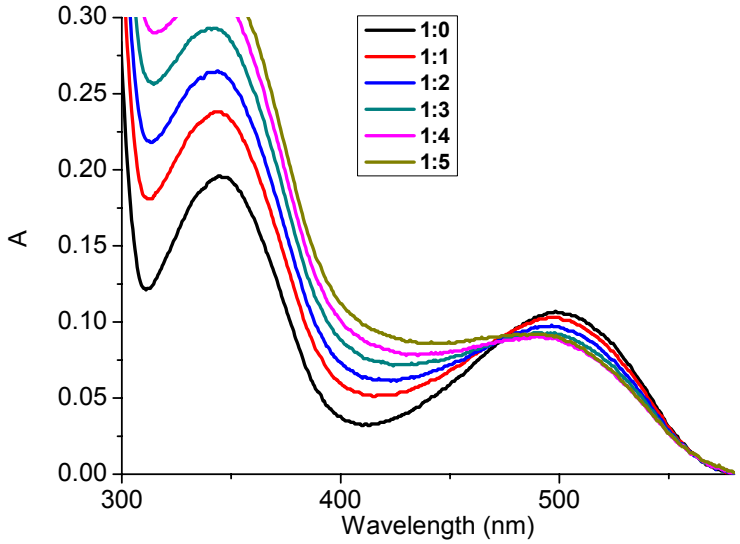


Fig. S8 Spectral results from the titration of HABA-STV complex with biotinylated DNA-G1 at pH 5.0 resulting in HABA release and a corresponding decrease in A_{500}.

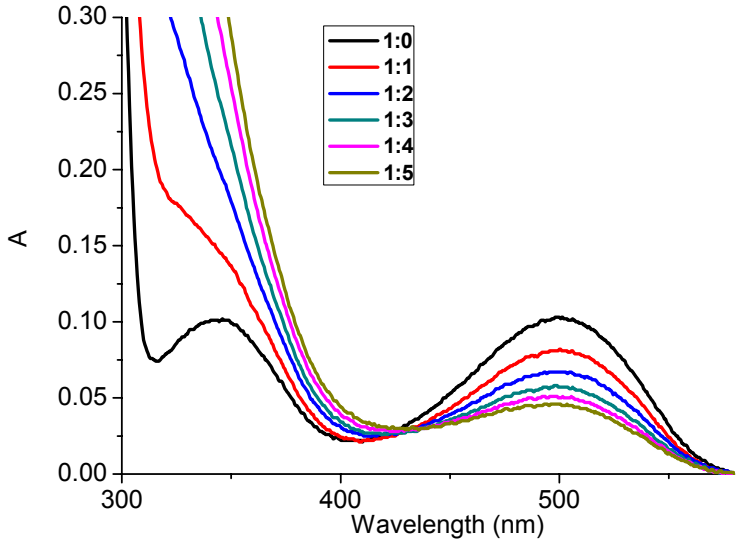


Fig. S9 Spectral results from the titration of HABA-STV complex with biotinylated DNA-G2 at pH 5.0 resulting in HABA release and a corresponding decrease in A_{500}.

11 Characterization of the STV-(DNA-G1)4 conjugate by CD spectroscopy

The conformational change of the $(G1\text{-}DNA)_4$-STV conjugate associated with the folded and extended states was examined by circular dichroism (CD) spectroscopy. The $(G1\text{-}DNA)_4$-STV conjugate (0.375 μM) was premixed with strand Y (1.5 μM) in pH 5.0 phosphate buffer. As shown in the **Fig. S10**, at pH 5.0 the CD spectrum showed the distinct characteristics of i-motif structure with a strong positive band near 285 nm, indicating that the system was in its folded state. While the pH value was increased to 8.0 by adding 1 M NaOH, the CD spectroscopy displayed the distinct characteristics of a B-form duplex DNA structure with a positive band near 275 nm, demonstrating the system was switched into its extended state. By adding HCl and NaOH alternatively and monitoring the amplitude of CD signal at 285 nm, the multiple cycling of the system could be achieved in a reliable manner (**Fig. S10**, inset).

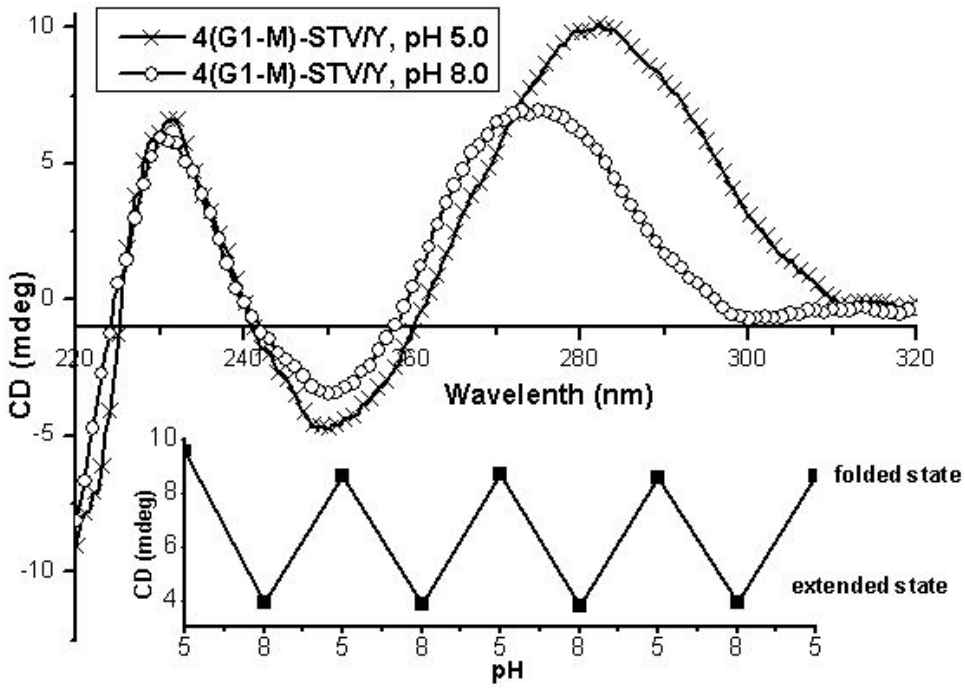
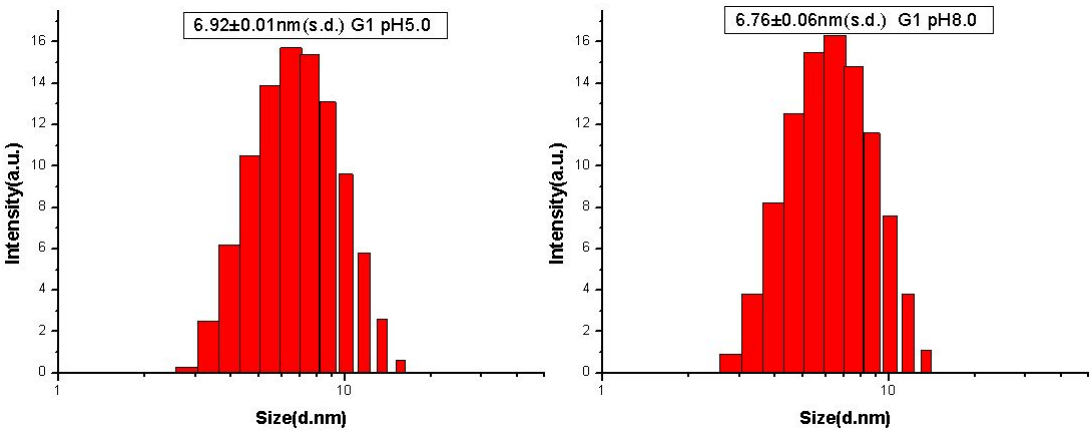


Fig.S10 Characterization of the STV-$(DNA\text{-}G1)_4$ conjugate by CD spectroscopy. Inset: cycling of the conformational switch of STV-$(DNA\text{-}G1)_4$ conjugate through measurement of the CD signal at 285 nm between pH 5.0 and pH 8.0 by adding NaOH or HCl alternatively.

12. Characterization of size change of STV-(DNA-G1)4 conjugate by dynamic light scattering (DLS)

Effective hydrodynamic diameter of the supramolecular system was measured by dynamic light scattering at 20 °C using a dynamic light scattering photometer (Nano ZS ZEN3600, Malvern Instruments Ltd., United Kingdom) equipped with laser at a wavelength of 633 nm. Dynamic light scattering (DLS) provides a direct measurement of the physical sizes of the sample particles. The dendrons G1(1 mM), STV(10 μM) and Dendrons-DNA-STV complex(1 μM) were respectively dissolved in the solution of 50 mM sodium phosphate (pH 5.0 and pH 8.0) and 100 mM NaCl. As shown in Fig.11, the apparent hydrodynamic diameters of dendrons and STV almost have no change at different pH. While it can be seen that in Fig. 12 the hydrodynamic volume of the G1-DNA-STV hybrid supramolecular system could been switched between the folded state and extended state, yielding effective hydrodynamic diameters of ~14.52±1.20 nm(s.d.) at pH 5.0 and ~20.27±2.00 nm(s.d.) at pH 8.0. The difference between the value (~6 nm) results from the two states controlled by conformation change of i-motif DNA.



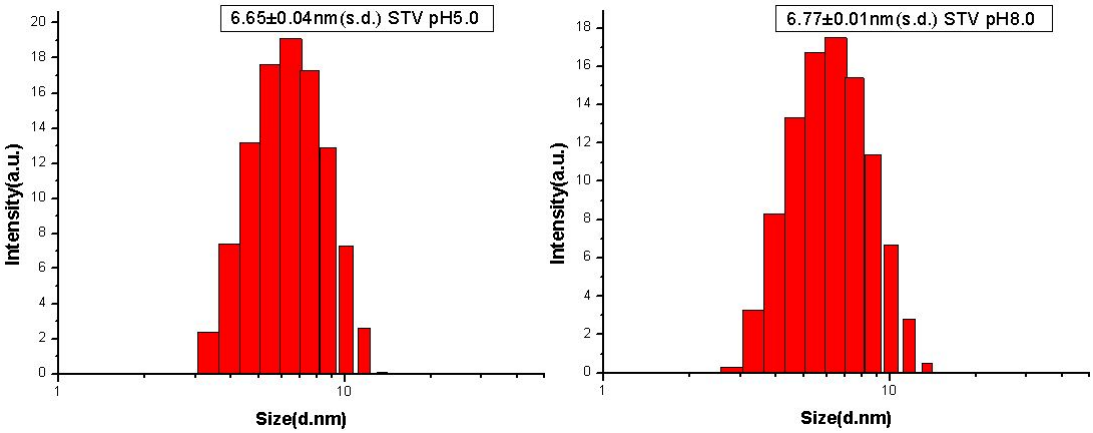


Fig.11 Size distribution by intensity graph as a histogram of the dendrons and STV measured by DLS.

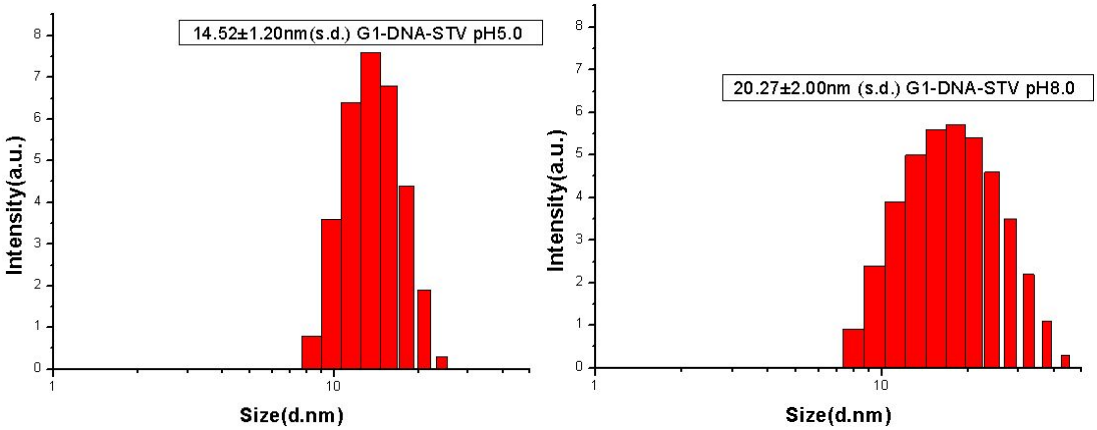
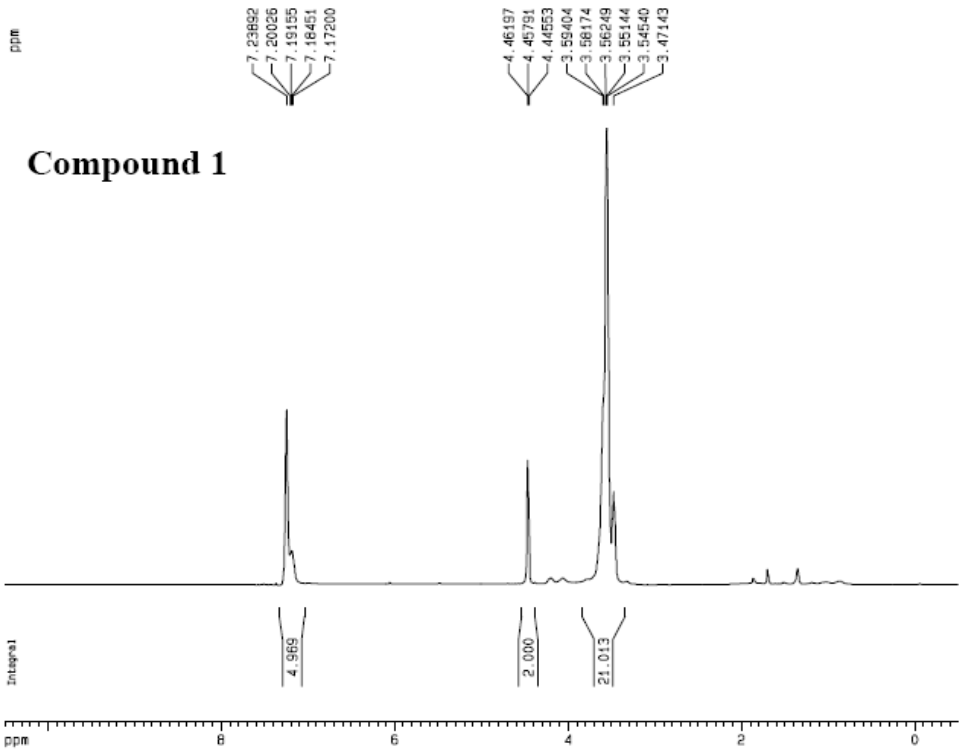
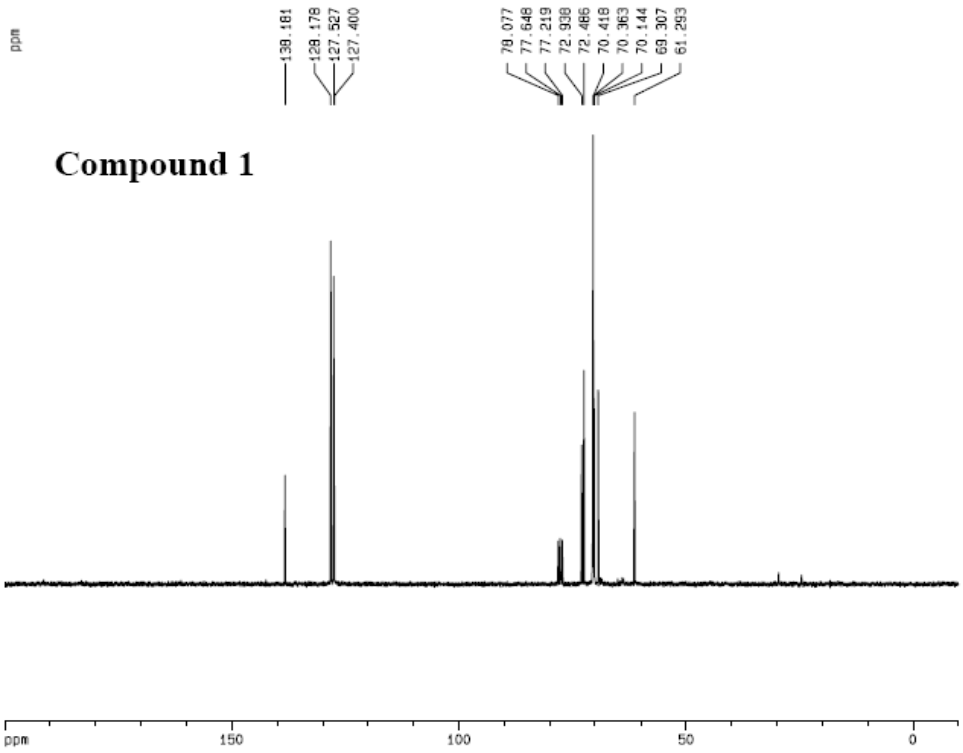
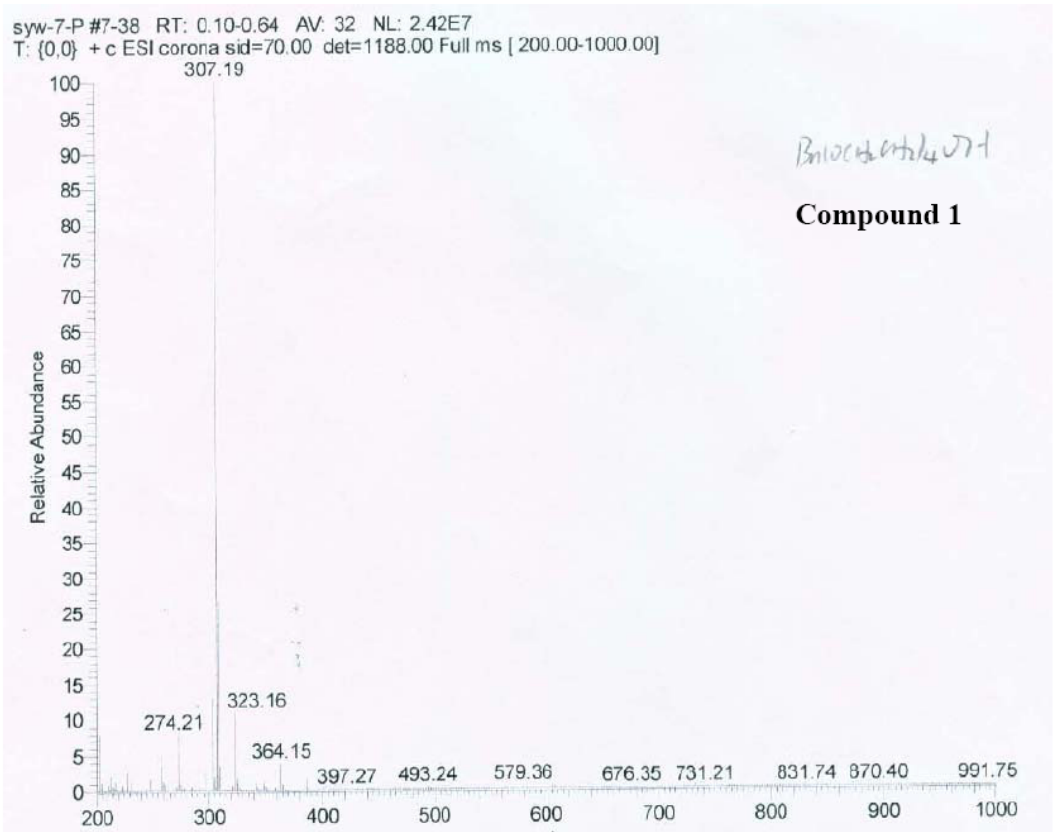


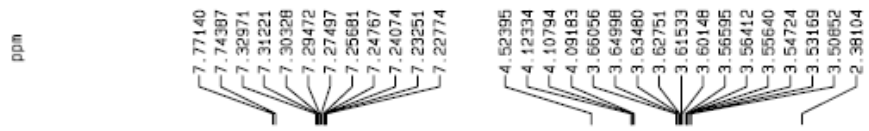
Fig.12 Size distribution by intensity graph as a histogram of the G1-DNA-STV complex measured by DLS.

13 ^{1}H and ^{13}C NMR Spectra of New Compounds

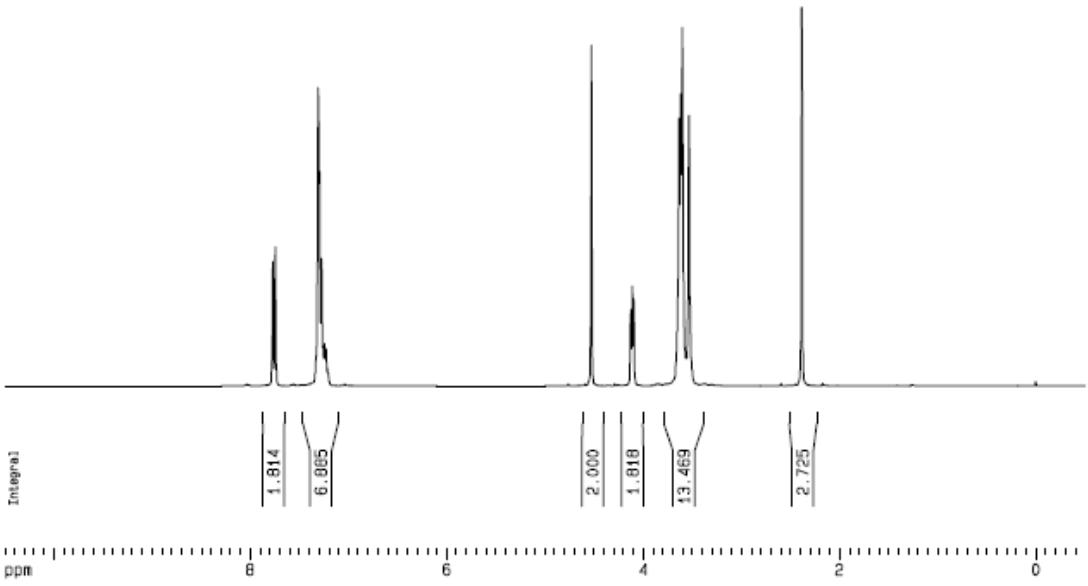


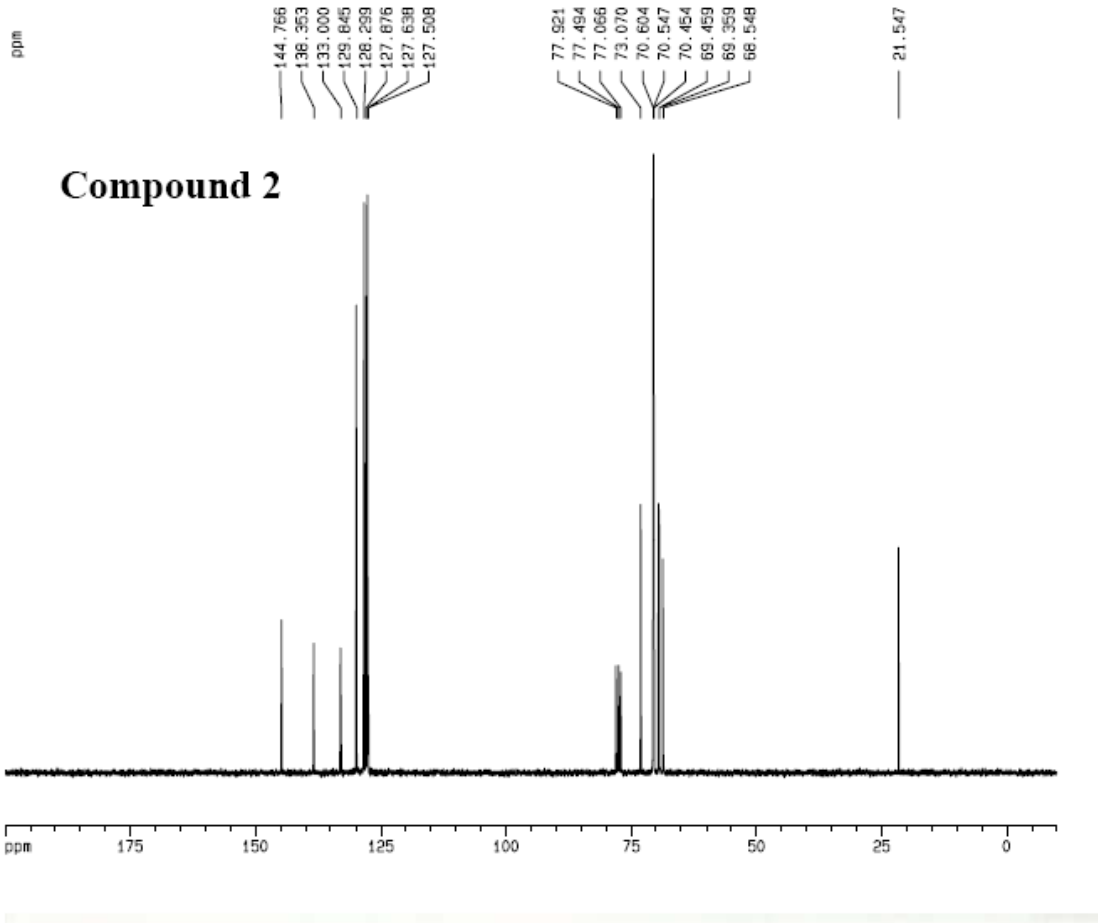


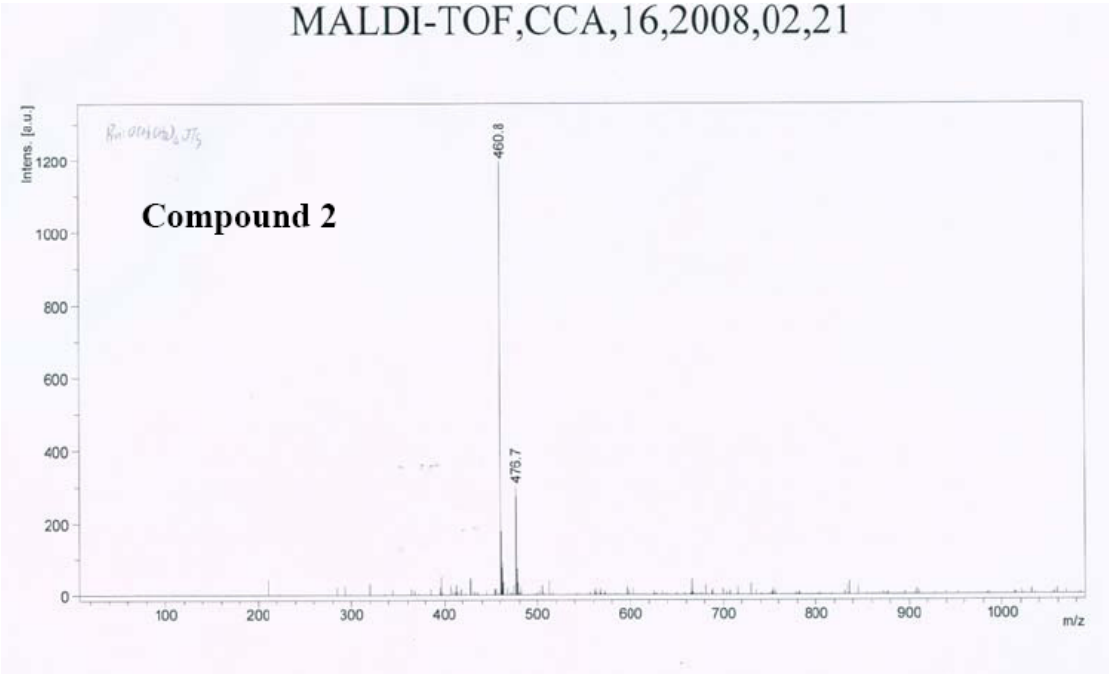

syw-7-P #7-38 RT: 0.10-0.64 AV: 32 NL: 2.42E7
T: {0,0} + c ESI corona sid=70.00 det=1188.00 Full ms [200.00-1000.00]
Relative Abundance
307.19
323.16
274.21
364.15
397.27
493.24
579.36
676.35
731.21
831.74
870.40
991.75
Compound 1

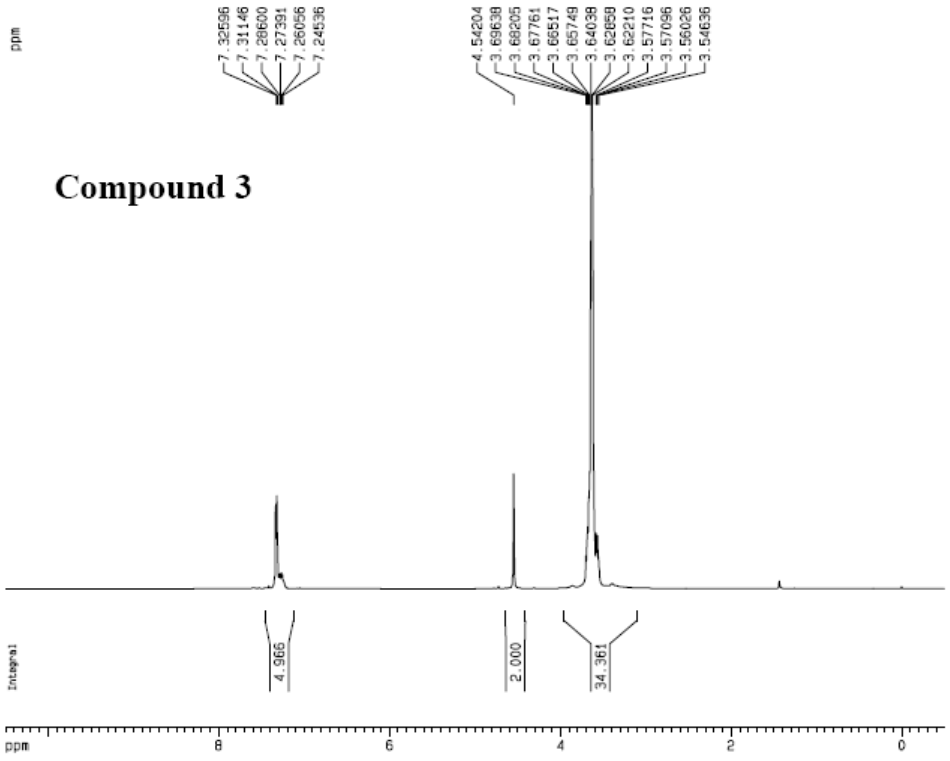

ppm
7.77140
7.74387
7.32971
7.31221
7.30328
7.29472
7.27497
7.25681
7.24767
7.24074
7.23251
7.22774
4.52395
4.12334
4.10794
4.09183
3.66056
3.64998
3.63480
3.62751
3.61533
3.60148
3.56595
3.56412
3.55640
3.54724
3.53169
3.50652
2.38104

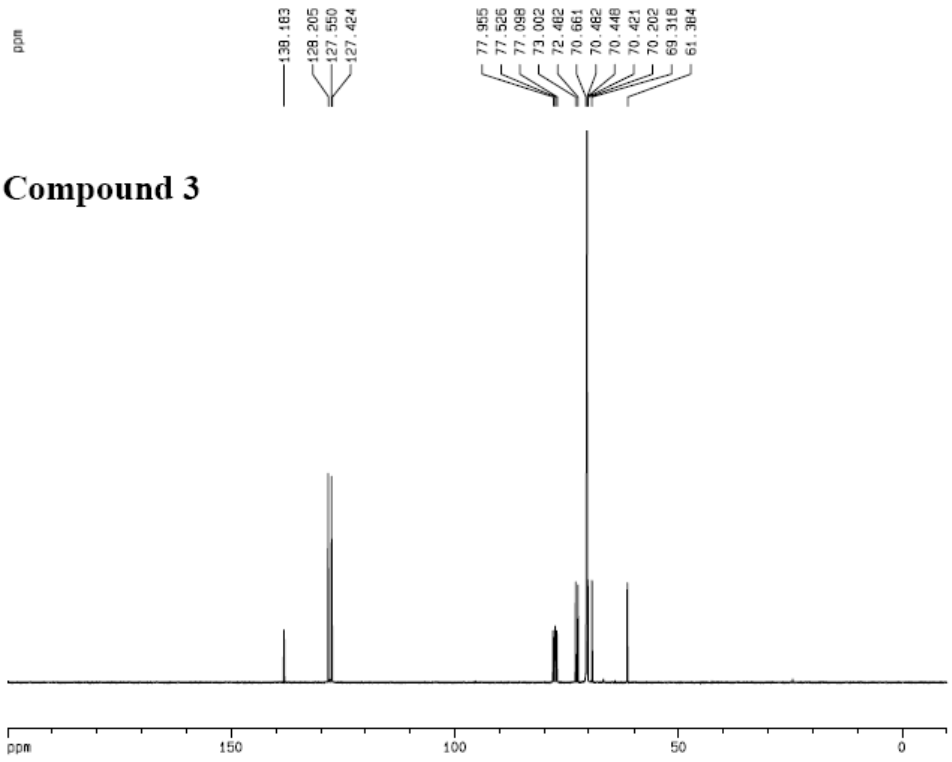
Compound 2

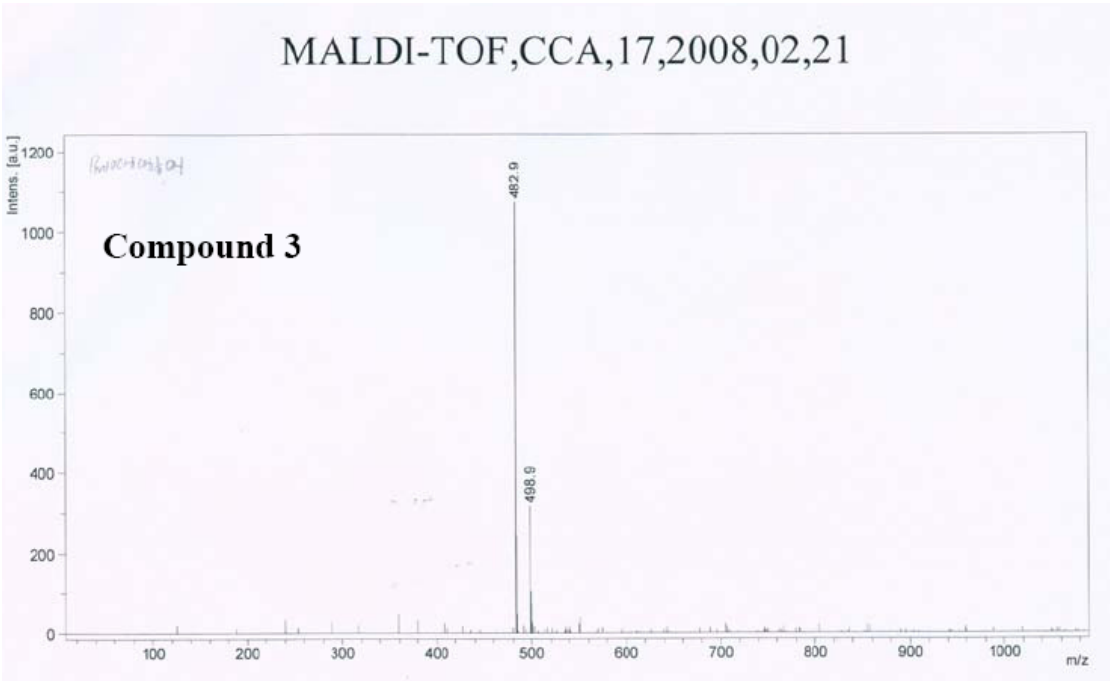

Integral
1.814
6.085
2.000
1.818
13.469
2.725
ppm
8
6
4
2
0


ppm
144.766
136.353
133.000
129.845
128.299
127.676
127.638
127.508
77.921
77.494
77.066
73.070
70.604
70.547
70.454
69.459
69.359
68.548
21.547
Compound 2
ppm
175
150
125
100
75
50
25
0


MALDI-TOF,CCA,16,2008,02,21
Intens. [a.u.]
Compound 2
460.8
476.7
1200
1000
800
600
400
200
0
100
200
300
400
500
600
700
800
900
1000
m/z

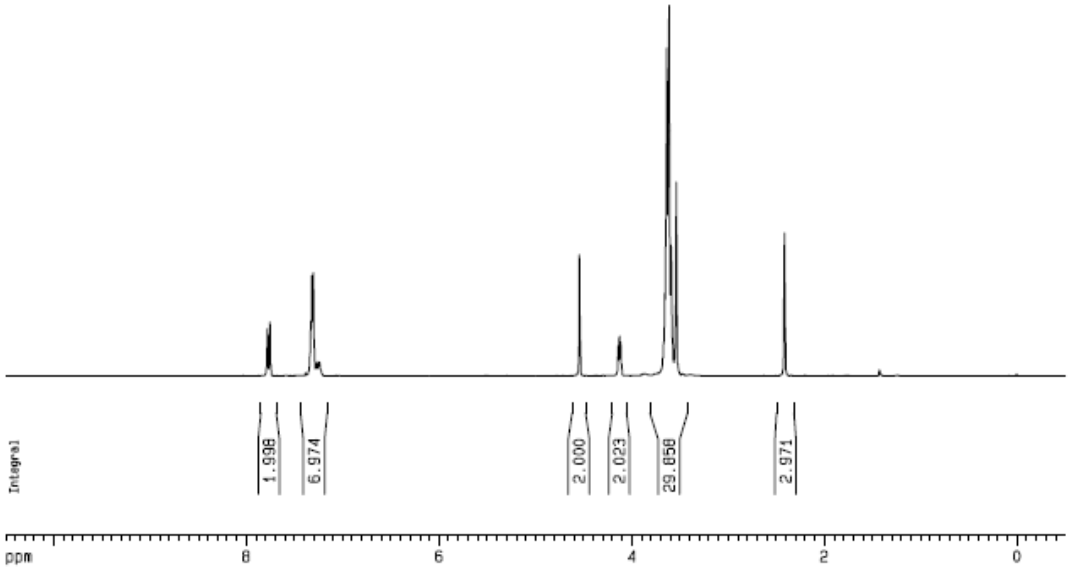

ppm
7.32596
7.31146
7.28600
7.27391
7.26056
7.24536
4.54204
3.69638
3.68205
3.67761
3.66517
3.65749
3.64039
3.62650
3.62210
3.57716
3.57096
3.56026
3.54636
Compound 3
Integral
4.966
2.000
34.361
ppm
8
6
4
2
0

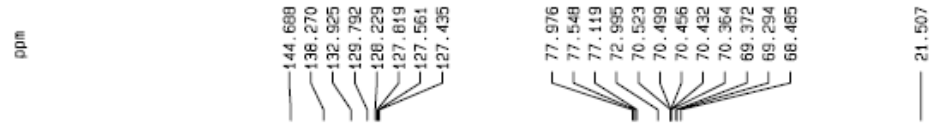

ppm
139.163
128.205
127.550
127.424
77.955
77.526
77.098
73.002
72.482
70.661
70.482
70.448
70.421
70.202
69.318
61.384
Compound 3
ppm
150
100
50
0


MALDI-TOF,CCA,17,2008,02,21
Compound 3
Intens. [a.u.]
482.9
498.9
m/z

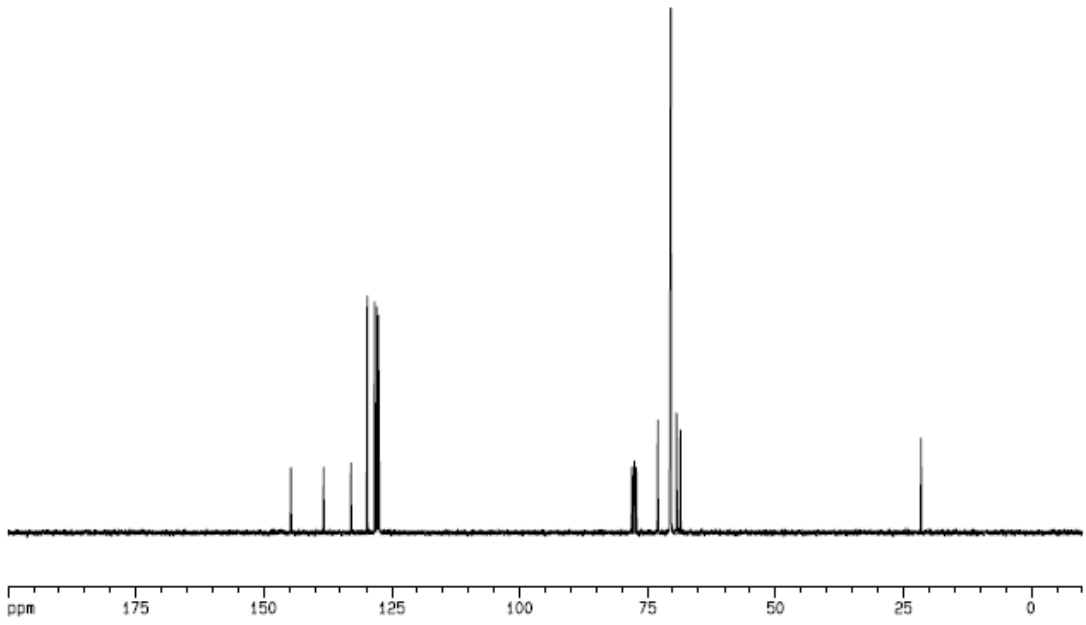

ppm
7.78166
7.77668
7.75402
7.33176
7.32060
7.31074
7.30400
4.53656
4.13880
4.12338
4.10733
3.66878
3.65182
3.63629
3.62332
3.61165
3.56842
3.53766
2.40853

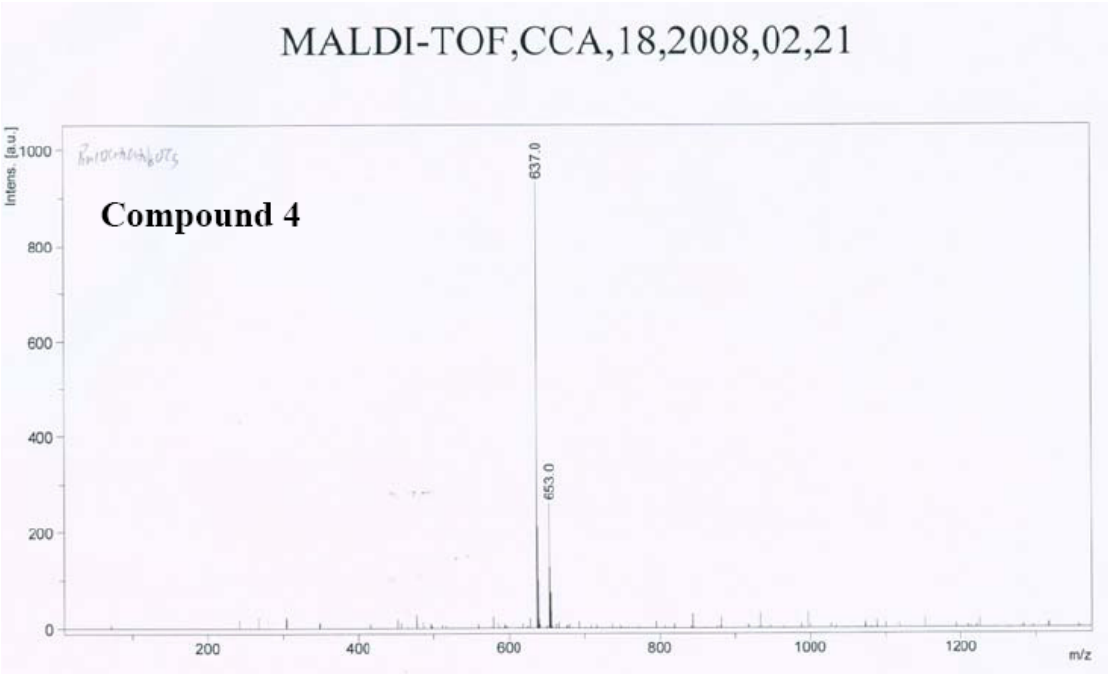
Compound 4

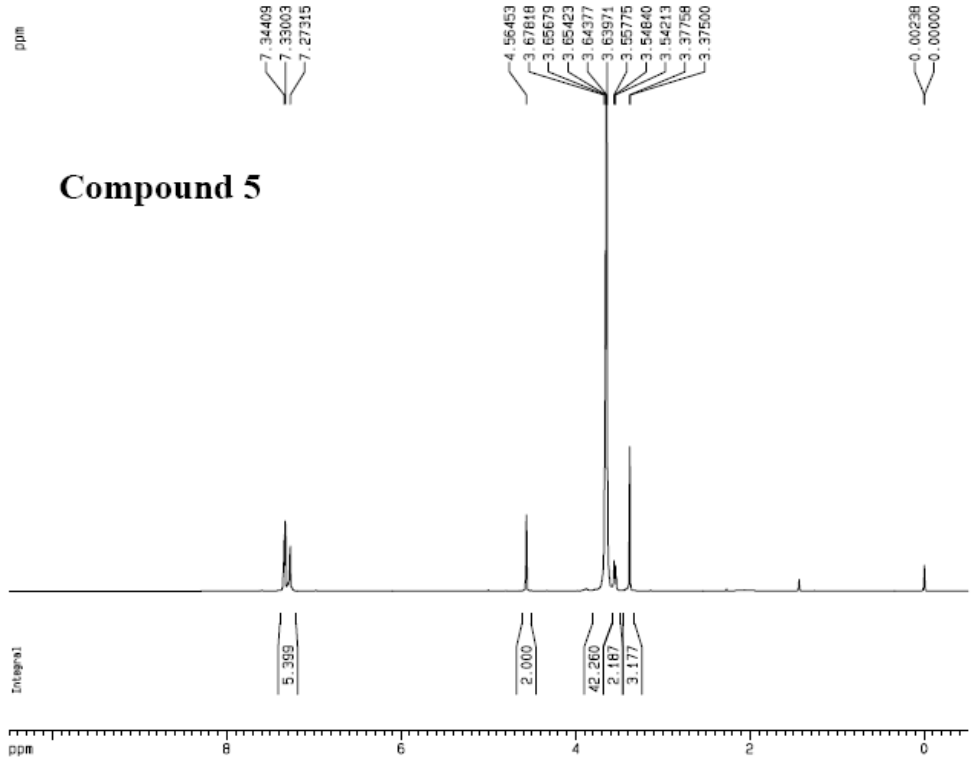

Integral
1.998
6.974
2.000
2.023
29.856
2.971
ppm
8
6
4
2
0

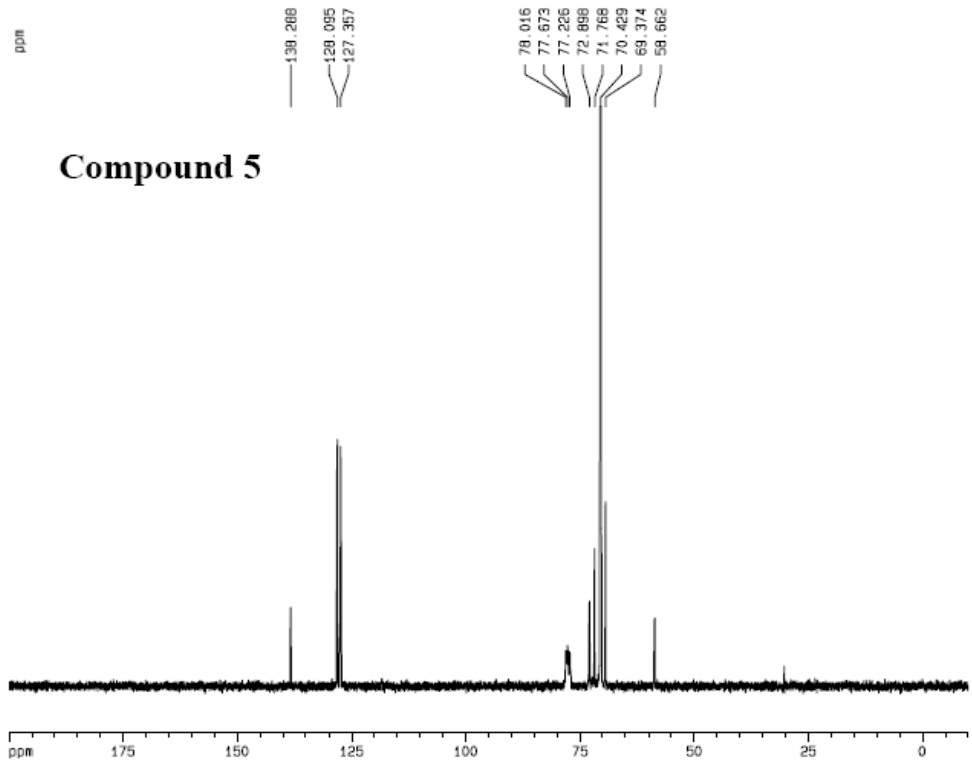

ppm
144.688
138.270
132.925
129.792
128.229
127.619
127.561
127.435
77.976
77.548
77.119
72.995
70.523
70.499
70.456
70.432
70.364
69.372
69.294
68.485
21.507

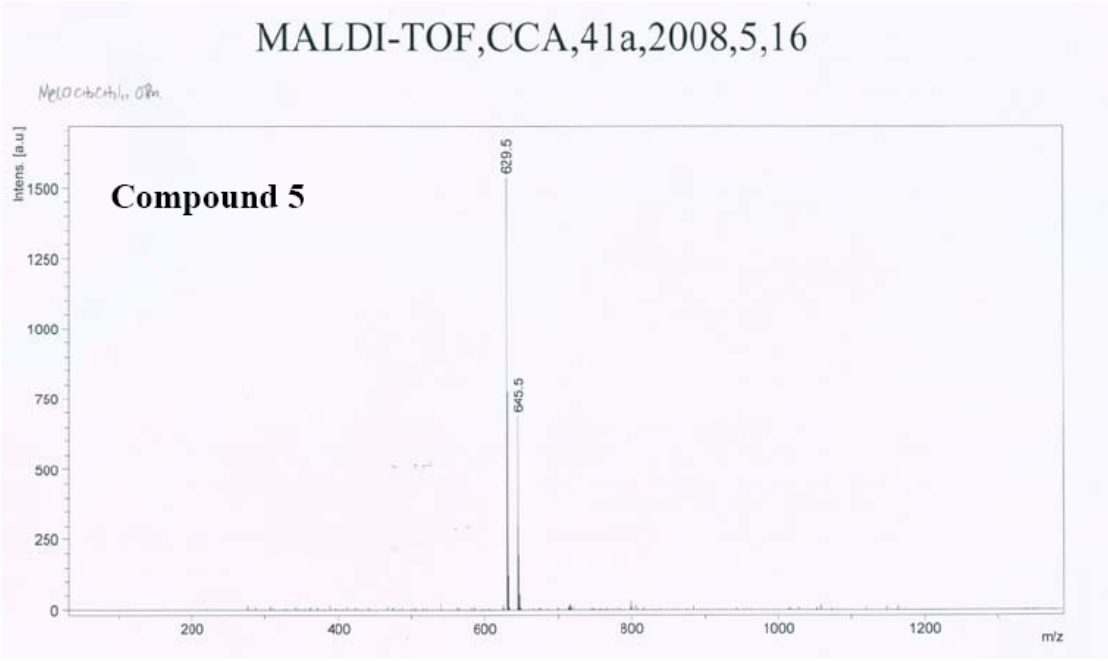
Compound 4

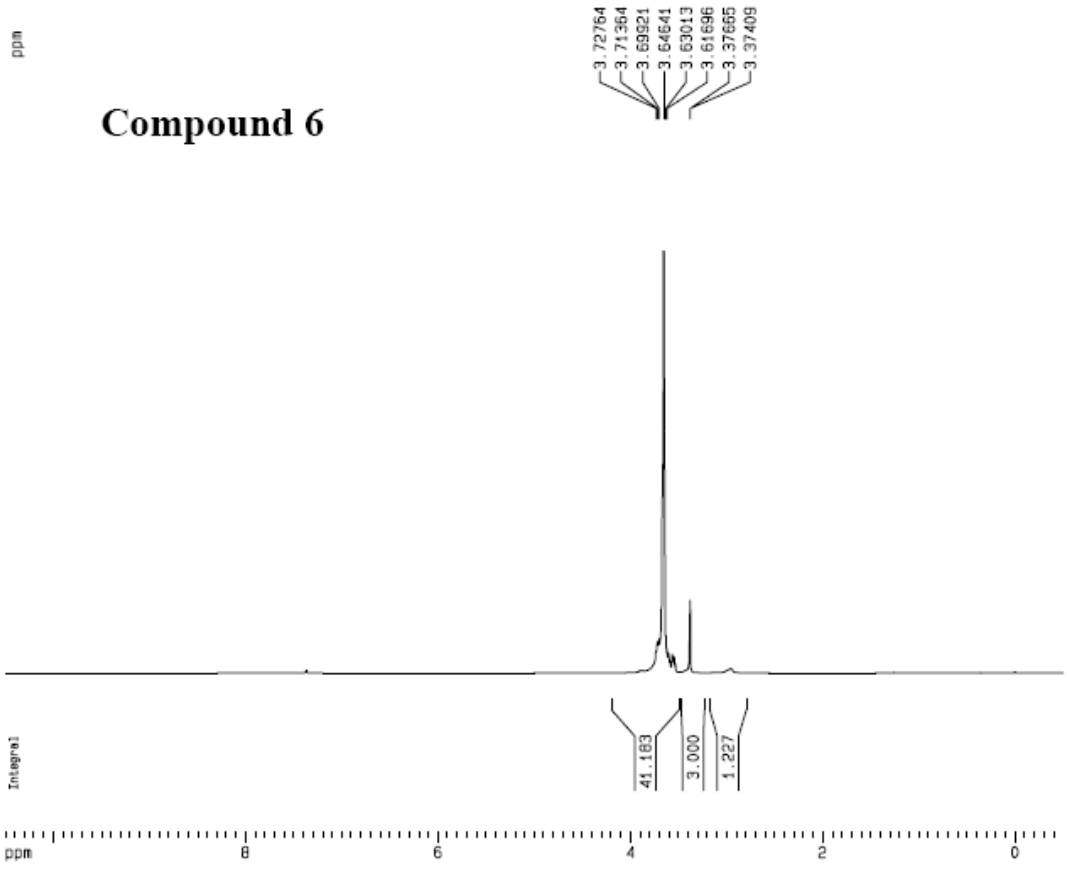

ppm
175
150
125
100
75
50
25
0

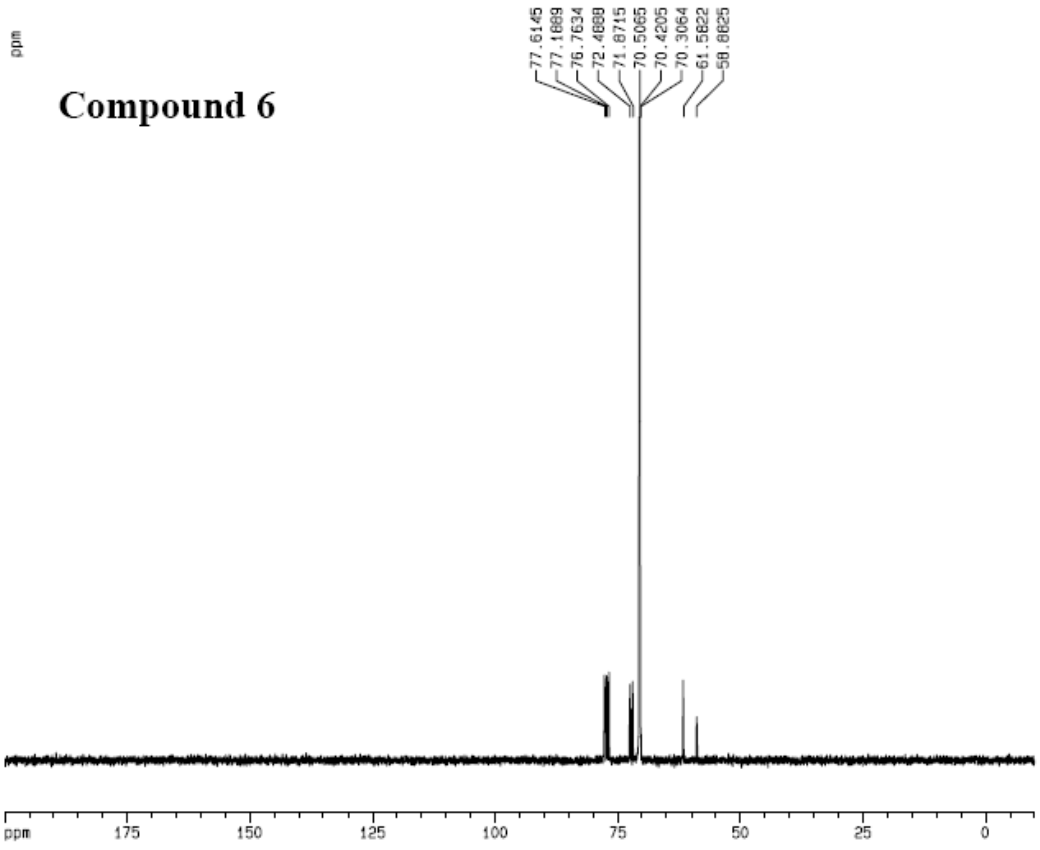

MALDI-TOF,CCA,18,2008,02,21
Compound 4
Intens. [a.u.]
1000
800
600
400
200
0
637.0
653.0
200
400
600
800
1000
1200
m/z

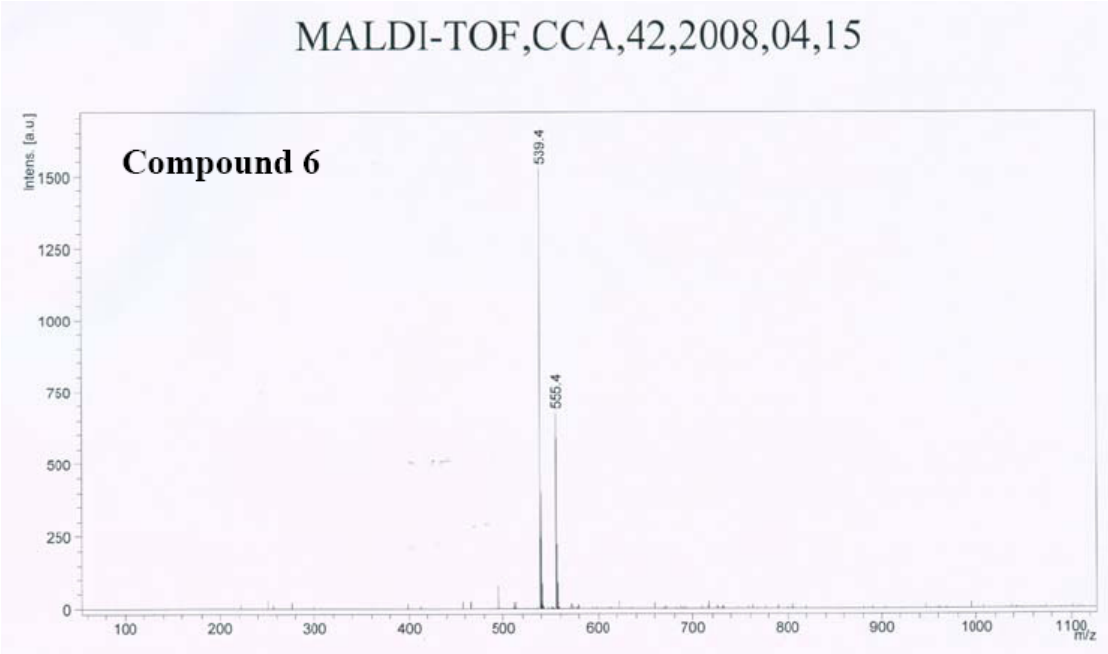

ppm
7.34409
7.33003
7.27315
4.56453
3.67818
3.65679
3.65423
3.64377
3.63971
3.55775
3.54840
3.54213
3.37758
3.37500
0.00238
0.00000
Compound 5
Integral
5.399
2.000
42.260
2.187
3.177
ppm
8
6
4
2
0

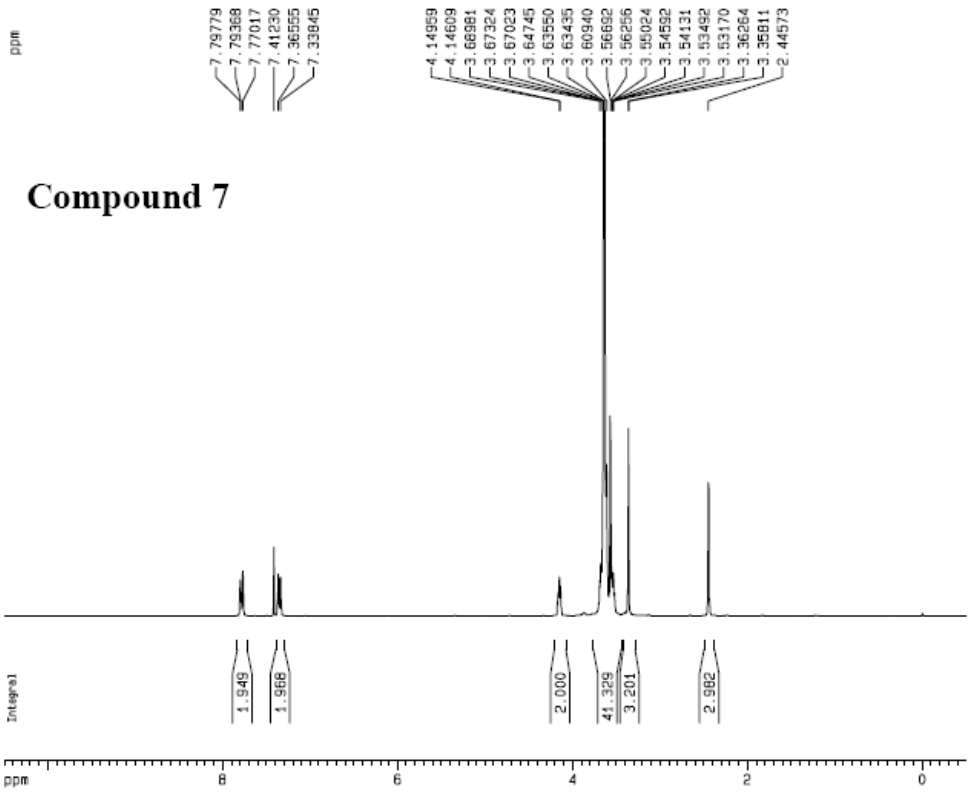

ppm
138.268
128.095
127.357
79.016
77.673
77.226
72.898
71.768
70.429
69.374
58.662
Compound 5
ppm
175
150
125
100
75
50
25
0

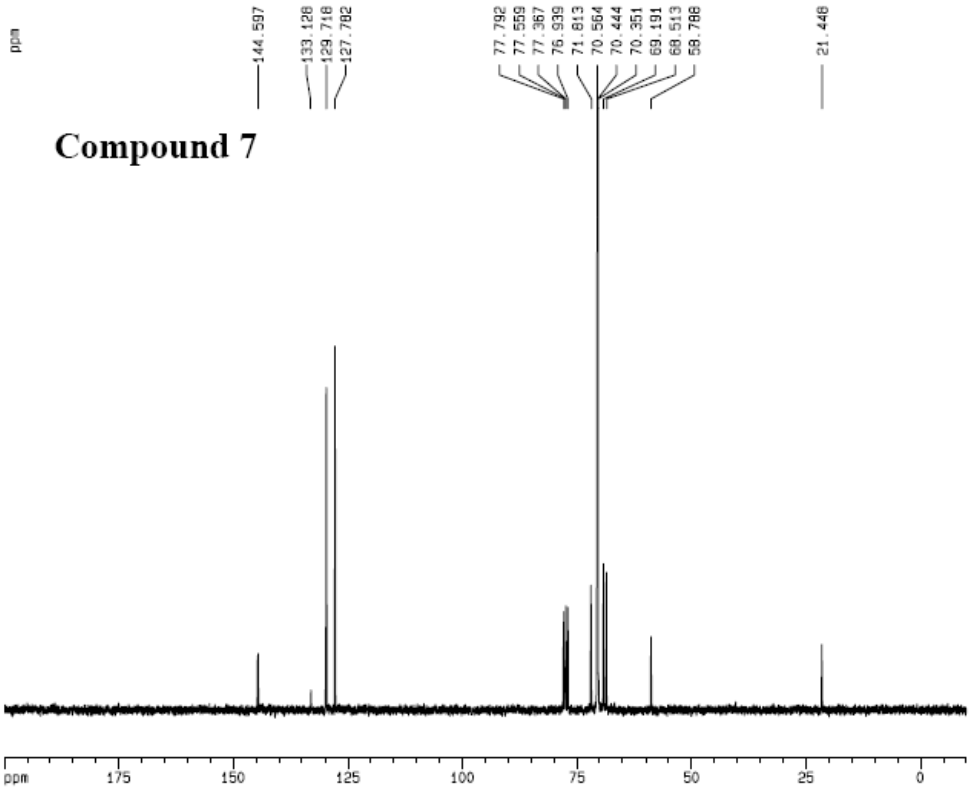

MALDI-TOF,CCA,41a,2008,5,16
Compound 5
Intens. [a.u.]
1500
1250
1000
750
500
250
0
629.5
645.5
200
400
600
800
1000
1200
m/z

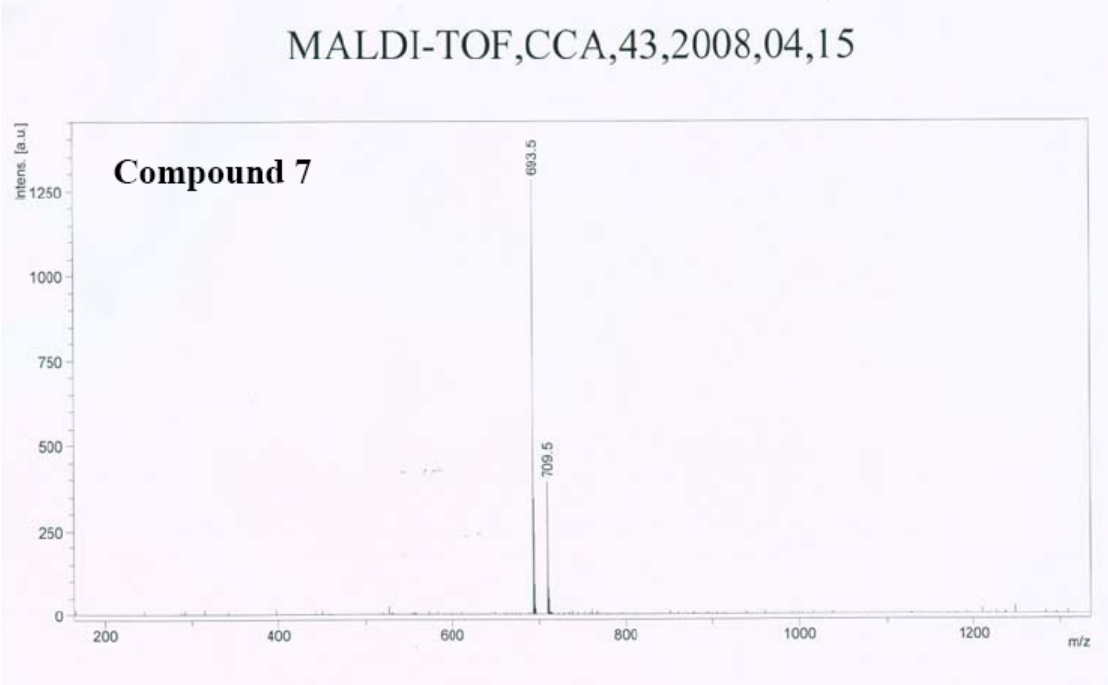

Compound 6
ppm
3.72764
3.71364
3.69921
3.64641
3.63013
3.61696
3.37665
3.37409
Integral
41.183
3.000
1.227
ppm
8
6
4
2
0

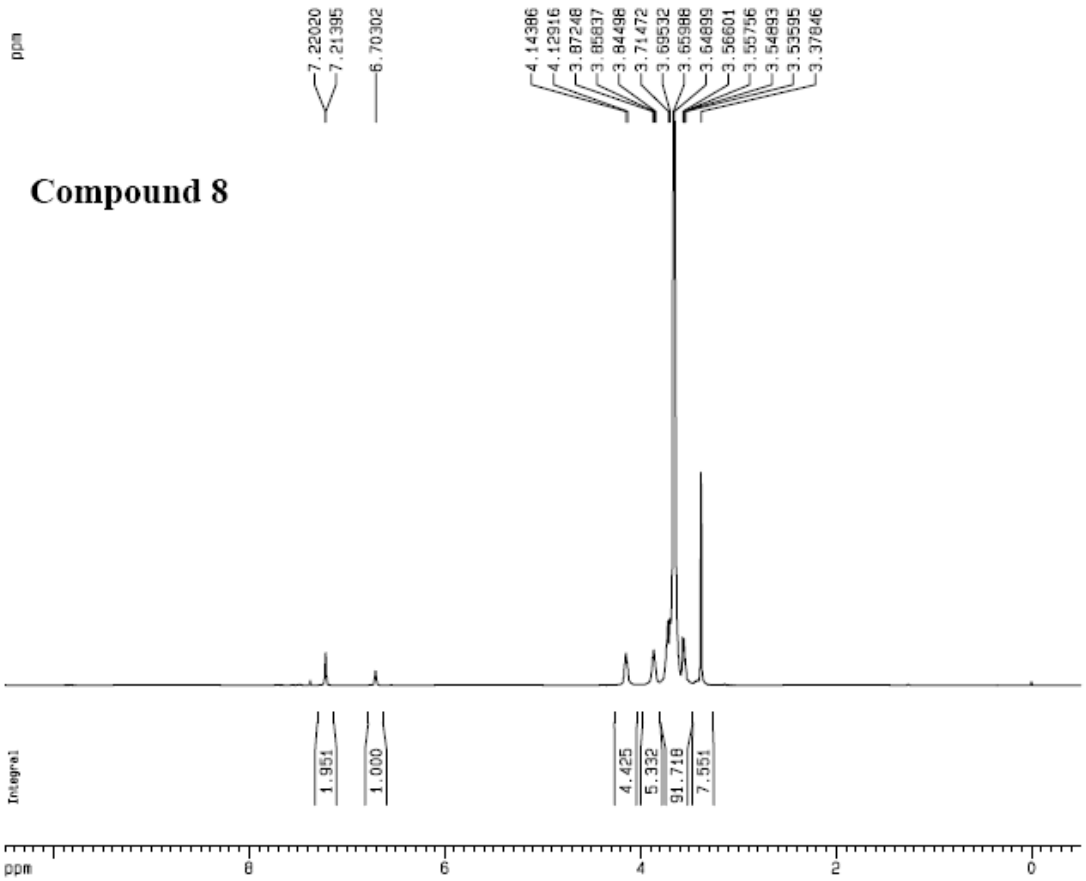

ppm
Compound 6
77.6145
77.1889
76.7634
72.4688
71.8715
70.5065
70.4205
70.3064
61.5822
58.8625
ppm
175
150
125
100
75
50
25
0

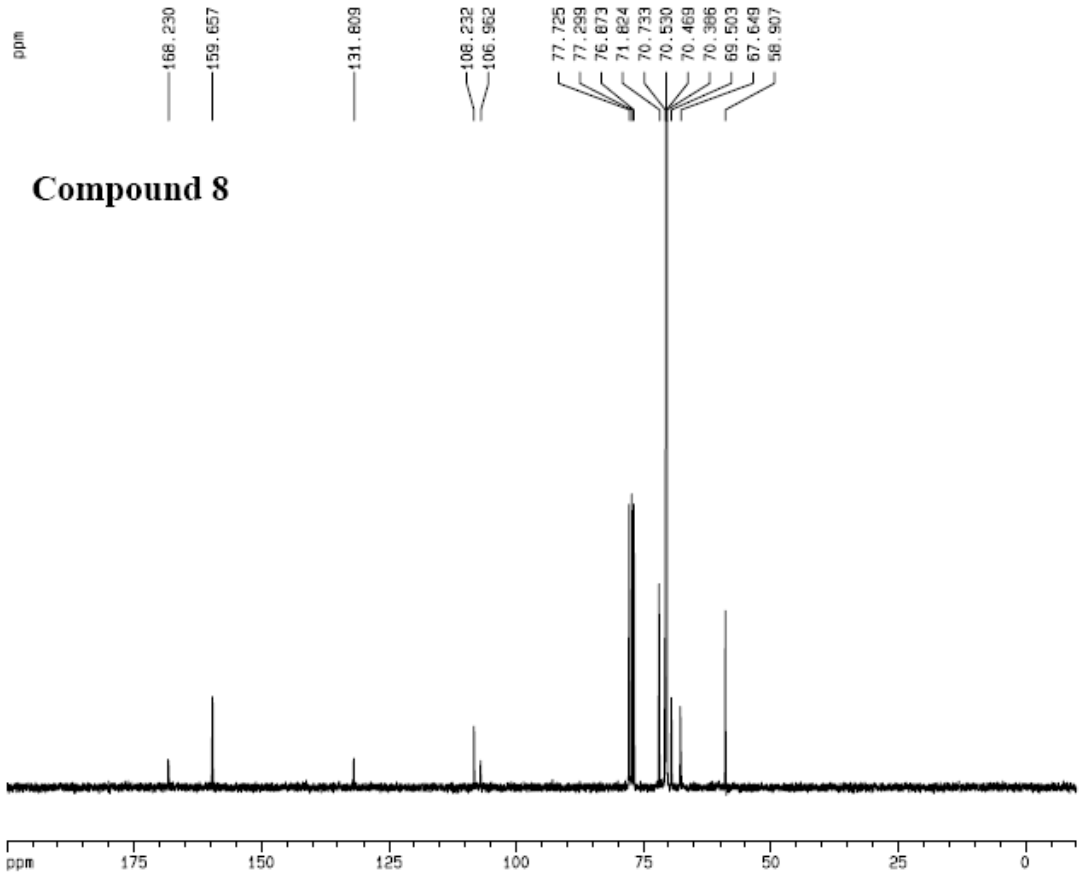

MALDI-TOF,CCA,42,2008,04,15
Compound 6
Intens. [a.u.]
1500
1250
1000
750
500
250
0
539.4
555.4
100
200
300
400
500
600
700
800
900
1000
1100
m/z

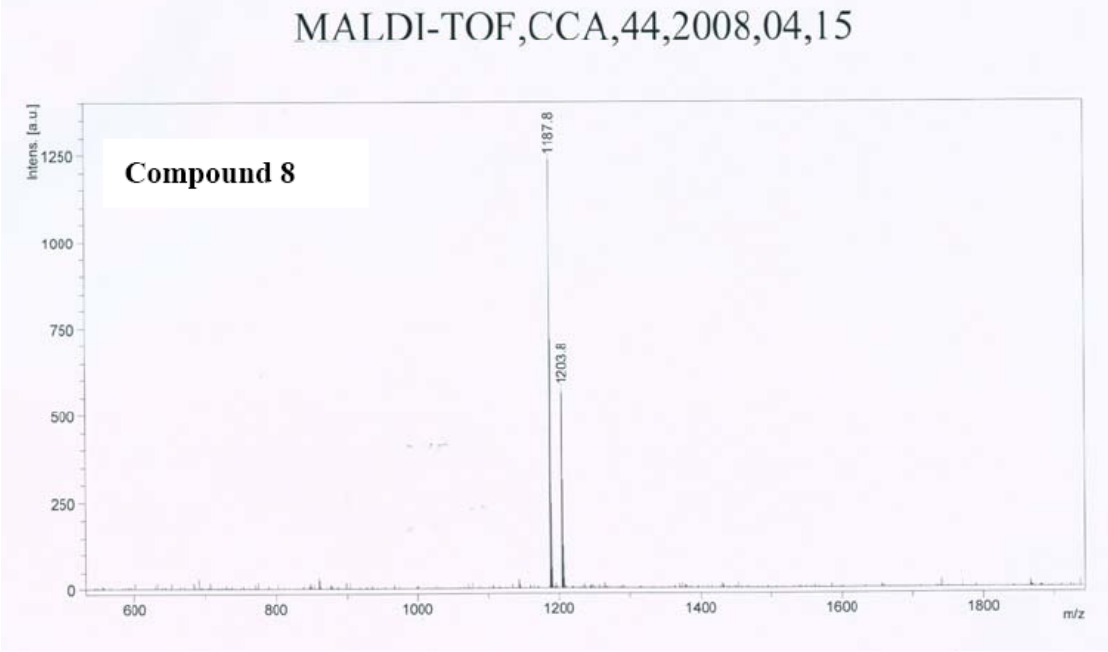

ppm
7.79779
7.79368
7.77017
7.41230
7.36555
7.33845
4.14959
4.14609
3.68981
3.67324
3.67023
3.64745
3.63550
3.63435
3.60940
3.56692
3.56256
3.55024
3.54592
3.54131
3.53492
3.53170
3.36264
3.35811
2.44573
Compound 7
Integral
1.949
1.966
2.000
41.329
3.201
2.982
ppm
8
6
4
2
0

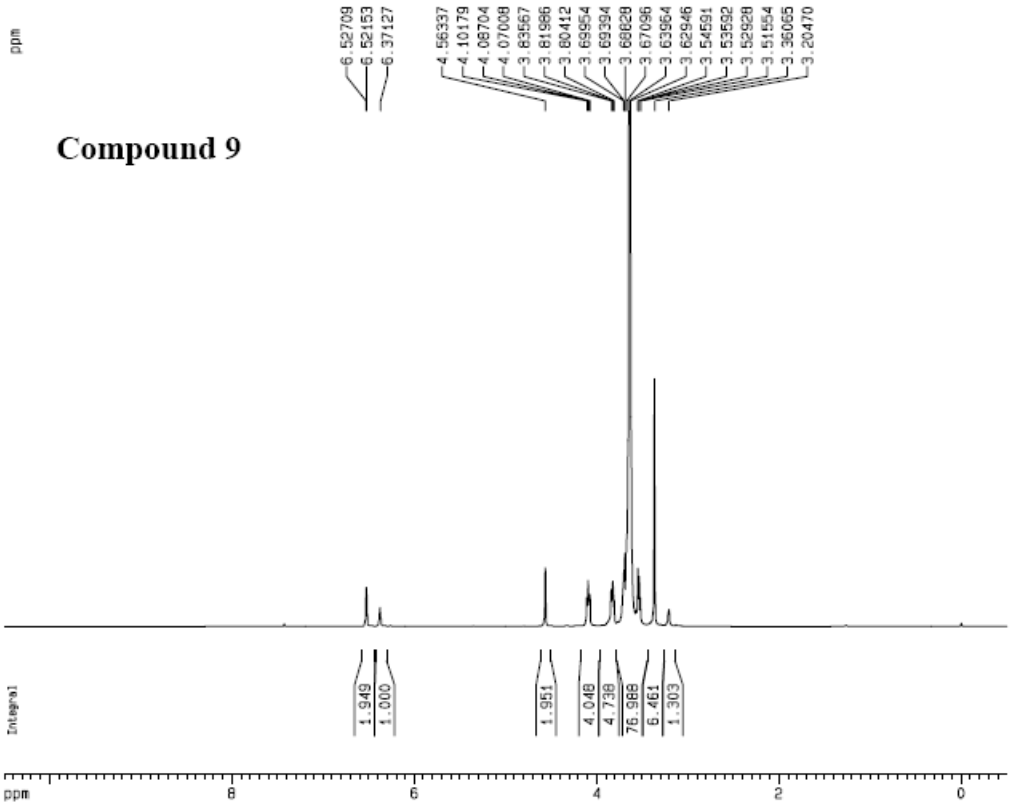

ppm
144.597
133.128
129.718
127.782
77.792
77.559
77.367
76.939
71.813
70.564
70.444
70.351
69.191
68.513
58.788
21.446
Compound 7
ppm
175
150
125
100
75
50
25
0

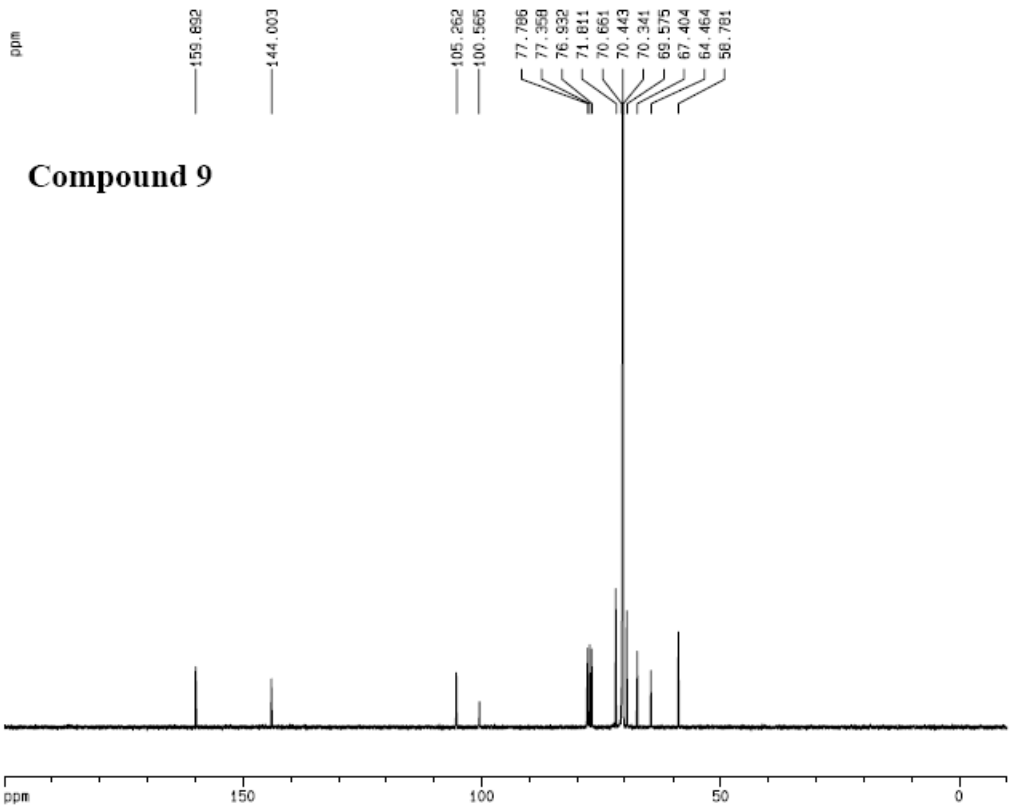

MALDI-TOF,CCA,43,2008,04,15
Compound 7
intens. [a.u.]
1250
1000
750
500
250
0
693.5
709.5
200
400
600
800
1000
1200
m/z

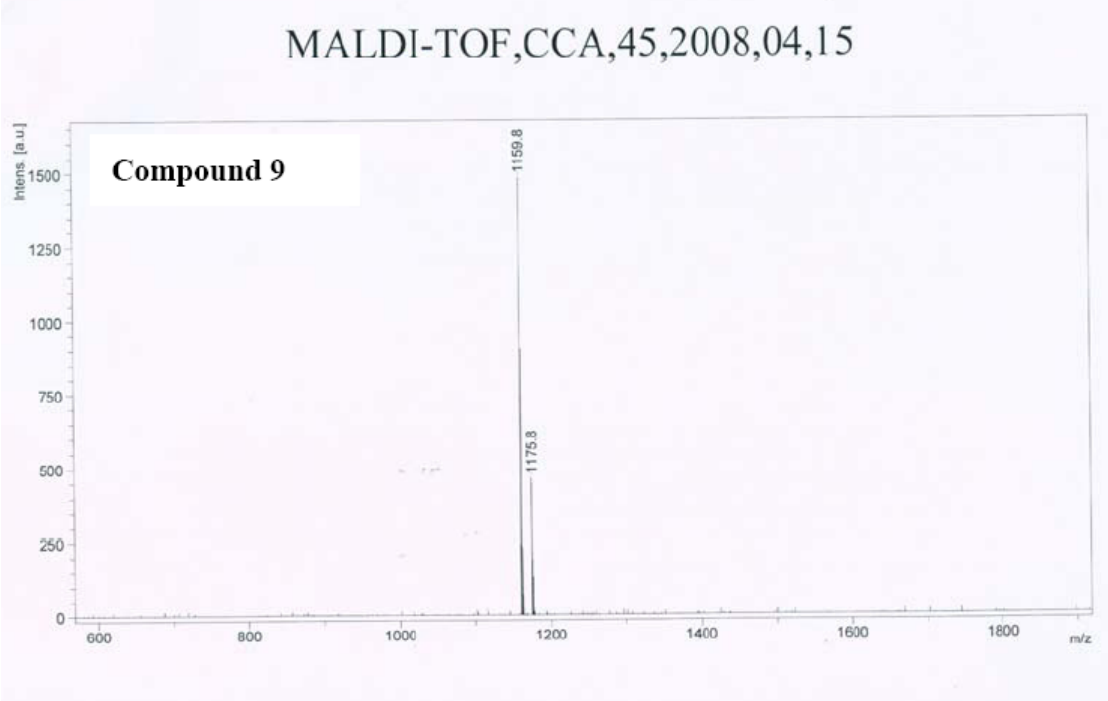

ppm
7.22020
7.21395
6.70302
4.14386
4.12916
3.87248
3.85837
3.84498
3.71472
3.69532
3.65988
3.64899
3.56601
3.55756
3.54893
3.53595
3.37846
Compound 8
Integral
1.951
1.000
4.425
5.332
91.718
7.551
ppm
8
6
4
2
0

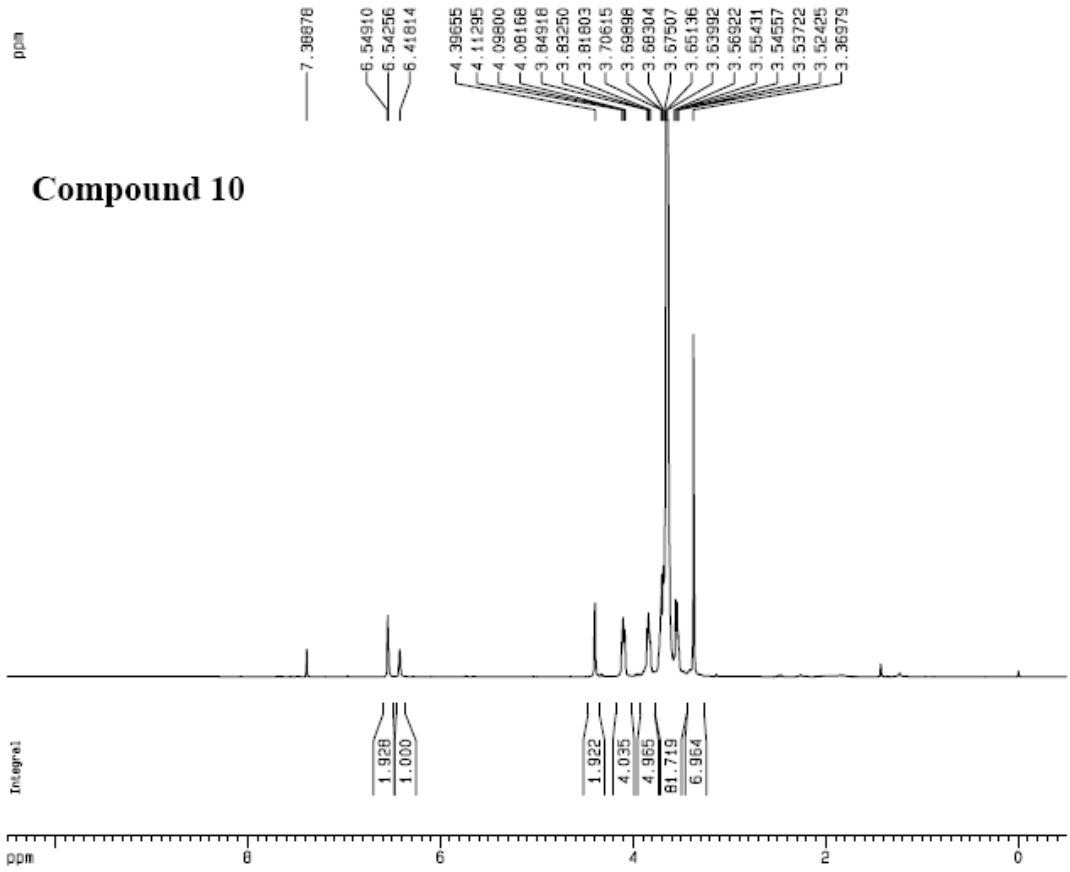

ppm
168.230
159.657
131.809
108.232
106.962
77.725
77.299
76.873
71.624
70.733
70.530
70.469
70.386
69.503
67.649
58.907
Compound 8
ppm
175
150
125
100
75
50
25
0

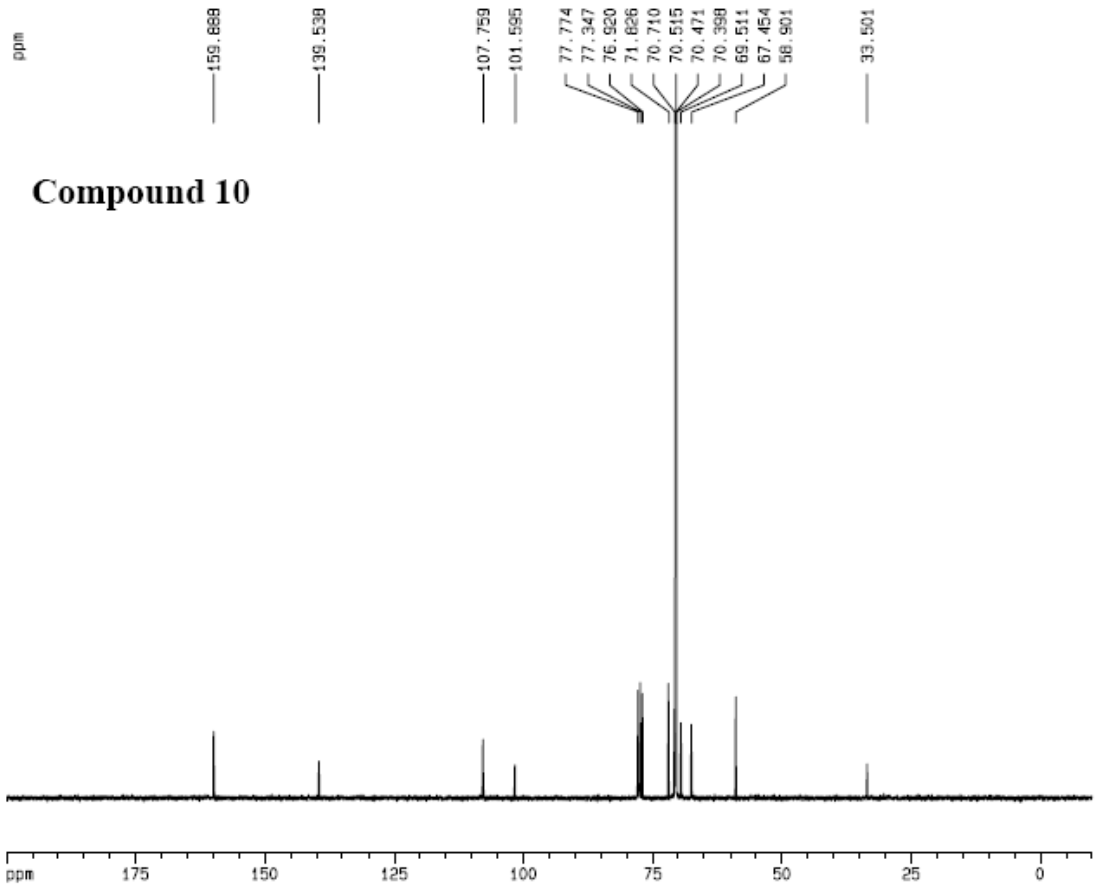

MALDI-TOF,CCA,44,2008,04,15
Intens. [a.u.]
Compound 8
1187.8
1203.8
1250
1000
750
500
250
0
600
800
1000
1200
1400
1600
1800
m/z

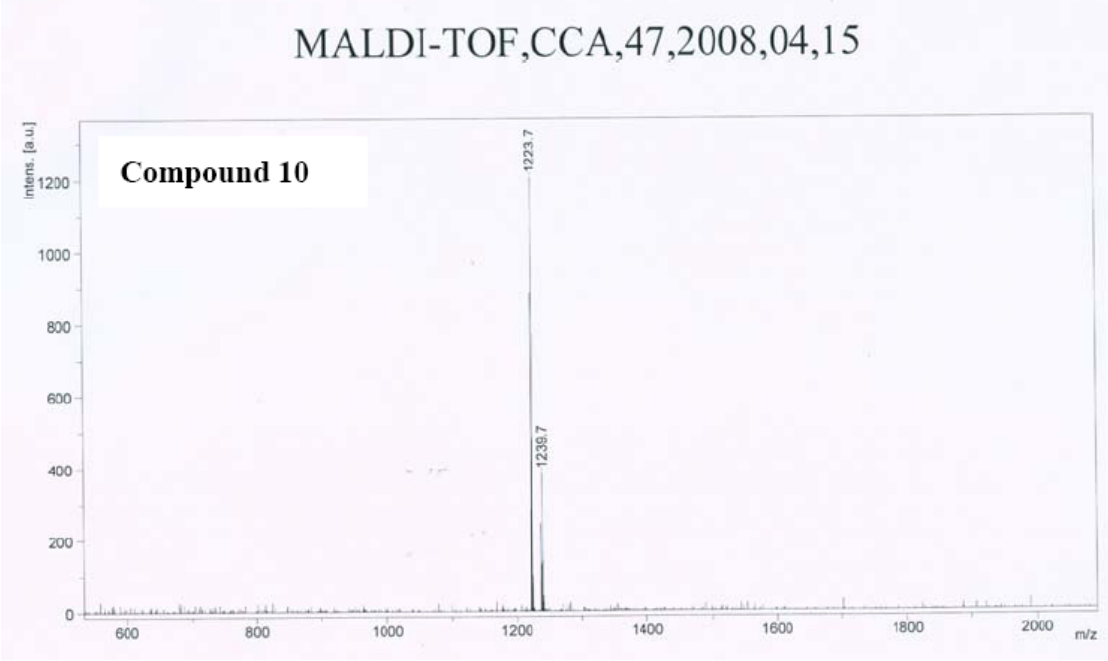

ppm
6.52709
6.52153
6.37127
4.56337
4.10179
4.08704
4.07008
3.83567
3.81986
3.80412
3.69954
3.69394
3.68828
3.67096
3.63964
3.62946
3.54591
3.53592
3.52928
3.51554
3.36065
3.20470
Compound 9
Integral
1.949
1.000
1.951
4.048
4.736
76.988
6.461
1.303
ppm
8
6
4
2
0


ppm
159.892
144.003
105.262
100.565
77.786
77.358
76.932
71.811
70.661
70.443
70.341
69.575
67.404
64.464
58.781
Compound 9
ppm
150
100
50
0


MALDI-TOF,CCA,45,2008,04,15
Compound 9
Intens [a.u.]
1159.8
1175.8
m/z

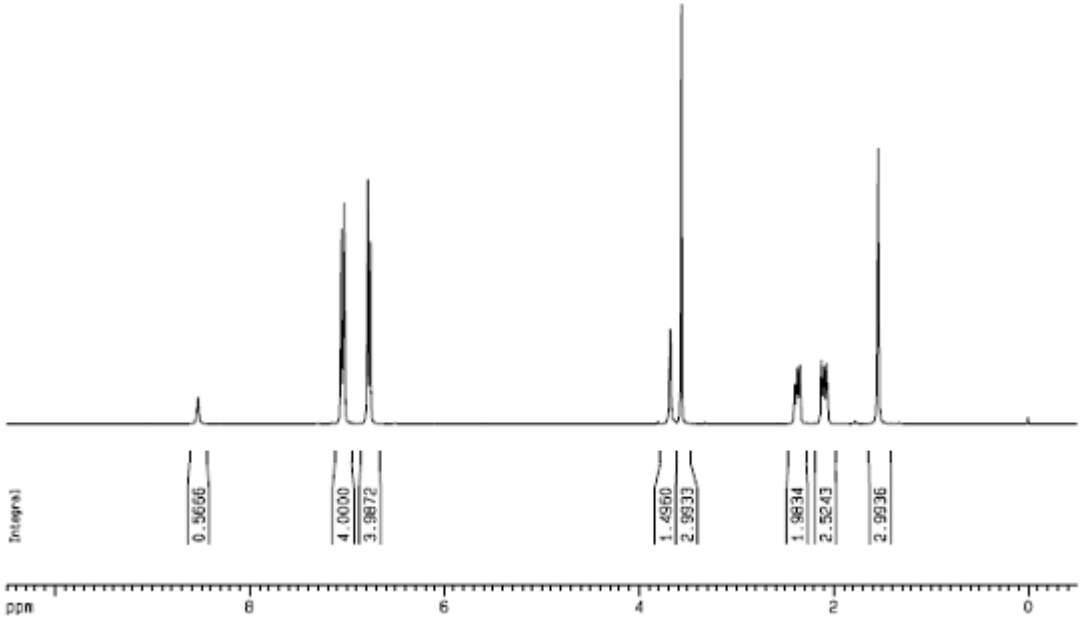

Compound 10
ppm
Integral
1.928
1.000
1.922
4.035
4.965
81.719
6.964


ppm
159.888
139.538
107.759
101.595
77.774
77.347
76.920
71.826
70.710
70.515
70.471
70.398
69.511
67.454
58.901
33.501
Compound 10
ppm
175
150
125
100
75
50
25
0


MALDI-TOF,CCA,47,2008,04,15
Compound 10
intens. [a.u.]
1223.7
1239.7
1200
1000
800
600
400
200
0
600
800
1000
1200
1400
1600
1800
2000
m/z

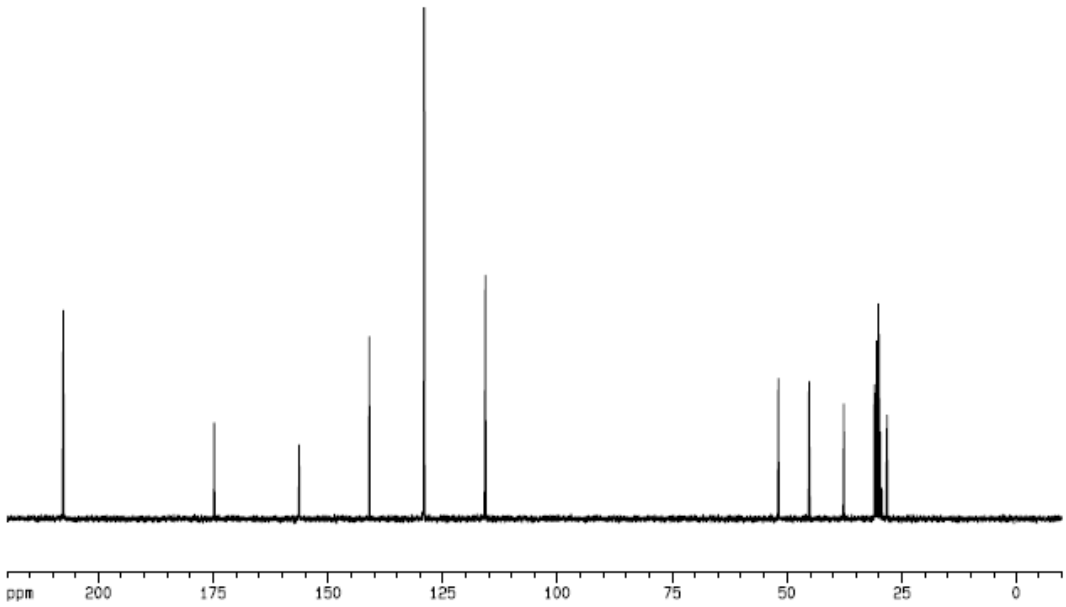

ppm
8.52556
7.05081
7.02168
6.78203
6.75300
3.67670
3.56481
3.56204
2.39488
2.37073
2.35861
2.34042
2.12349
2.11197
2.10313
2.09527
2.06935
2.06732
2.05968
2.05224
1.53997

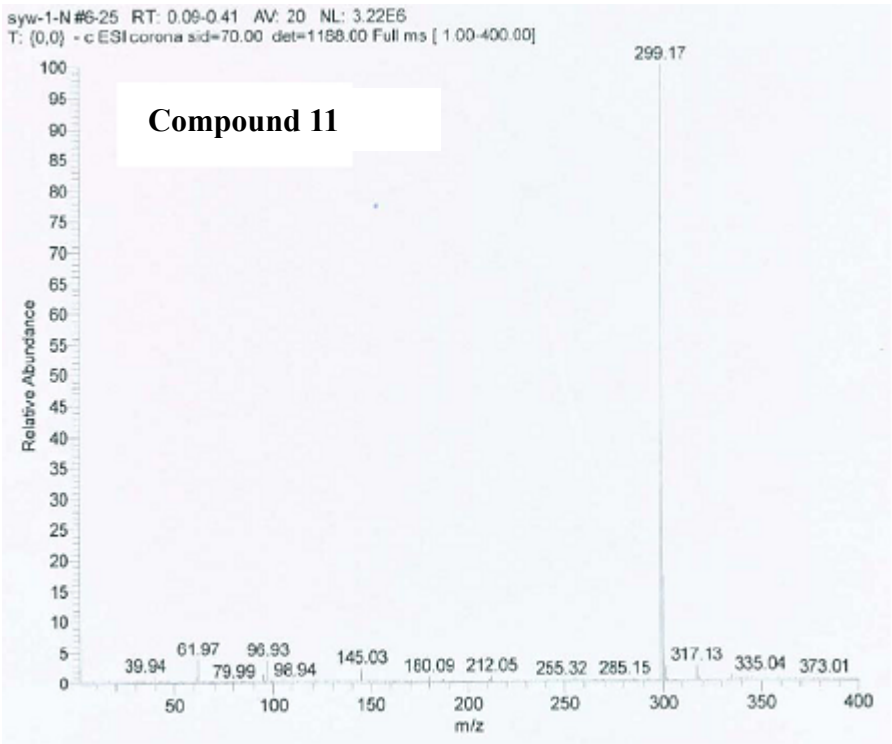
Compound 11

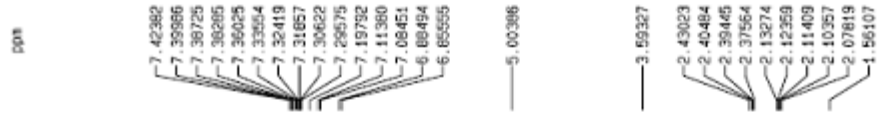

Integral
0.5666
4.0000
3.9872
1.4960
2.9933
1.9834
2.5243
2.9936
ppm
8
6
4
2
0


ppm
207.552
174.785
156.148
156.049
140.896
129.016
115.668
115.591
51.781
45.038
37.567
30.790
30.703
30.533
30.276
30.020
29.763
29.506
29.249
28.113

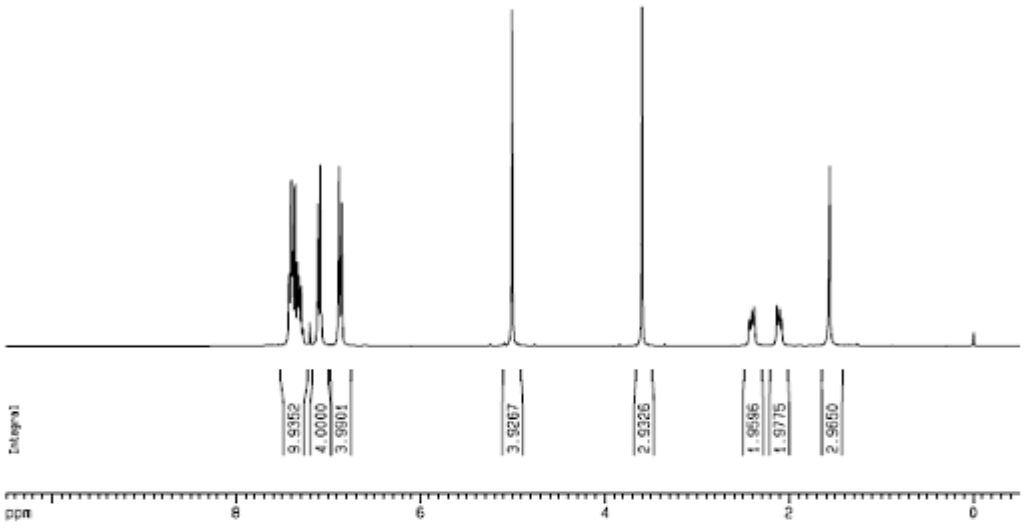
Compound 11

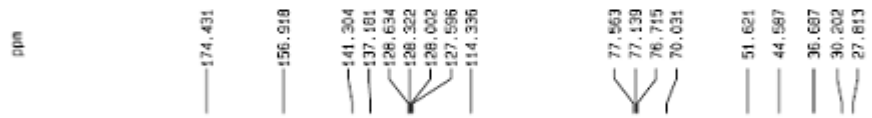

ppm
200
175
150
125
100
75
50
25
0


syw-1-N #6-25 RT: 0.09-0.41 AV: 20 NL: 3.22E6
T: {0,0} - c ESI corona sid=70.00 det=1188.00 Full ms [1.00-400.00]
Compound 11
299.17
Relative Abundance
m/z
39.94
61.97
79.99
96.93
98.94
145.03
160.09
212.05
255.32
285.15
317.13
335.04
373.01

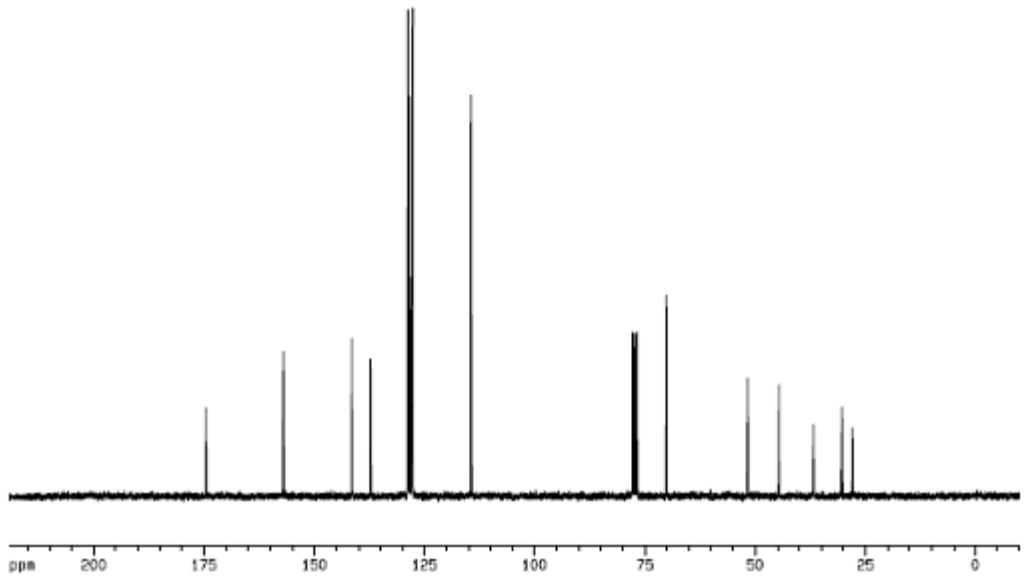


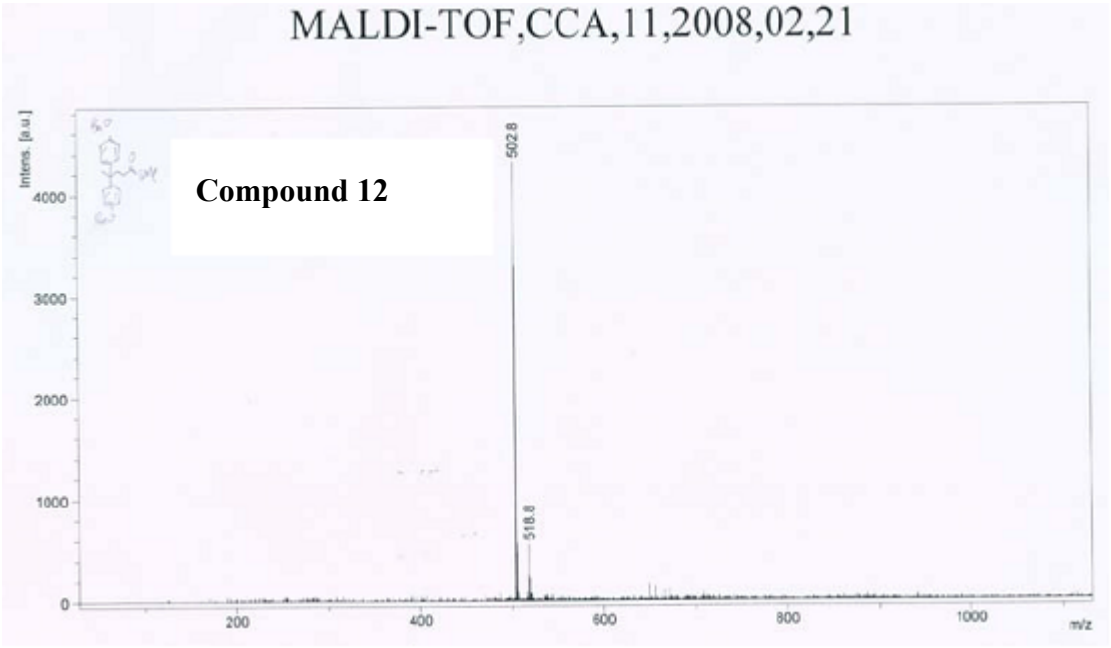
Compound 12

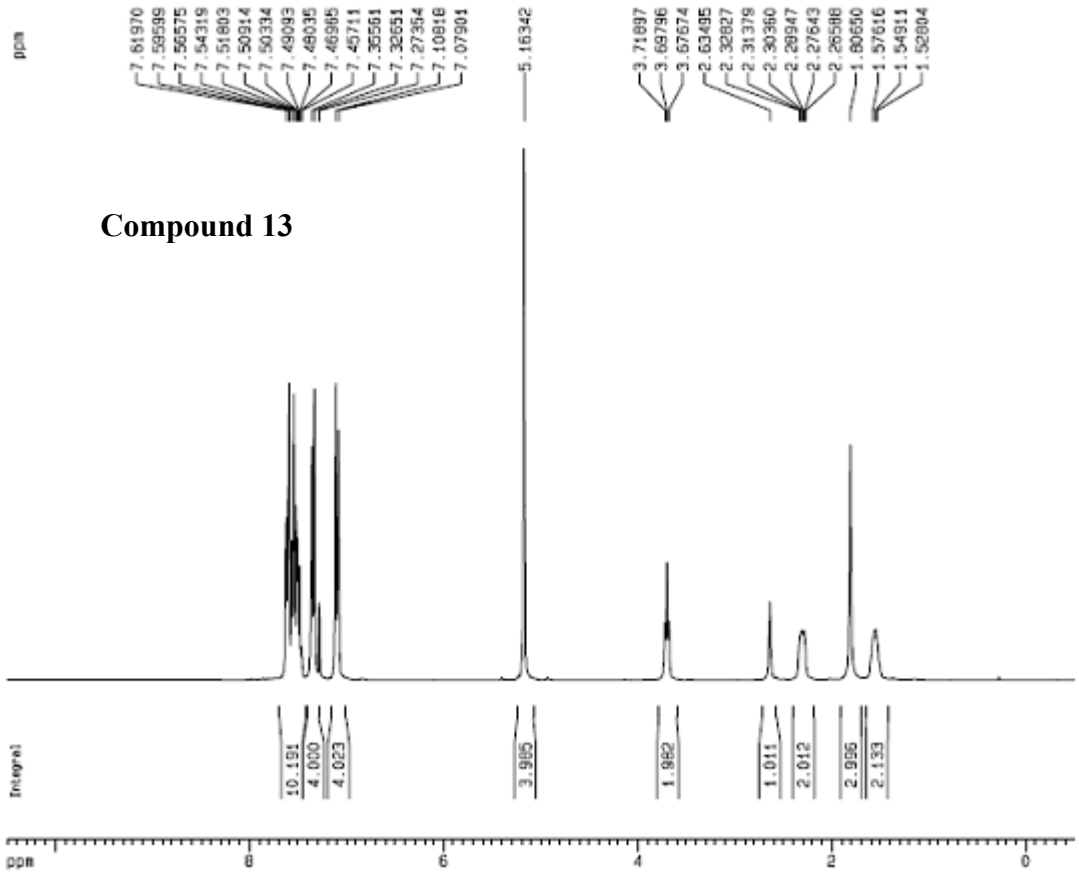


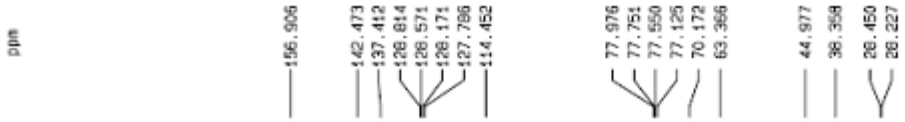


Compound 12

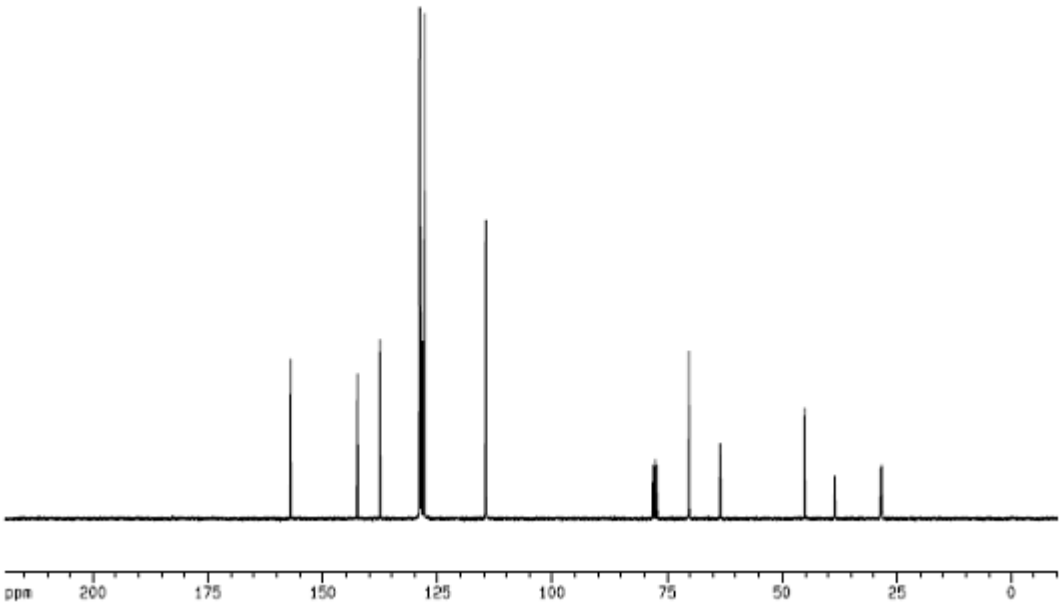


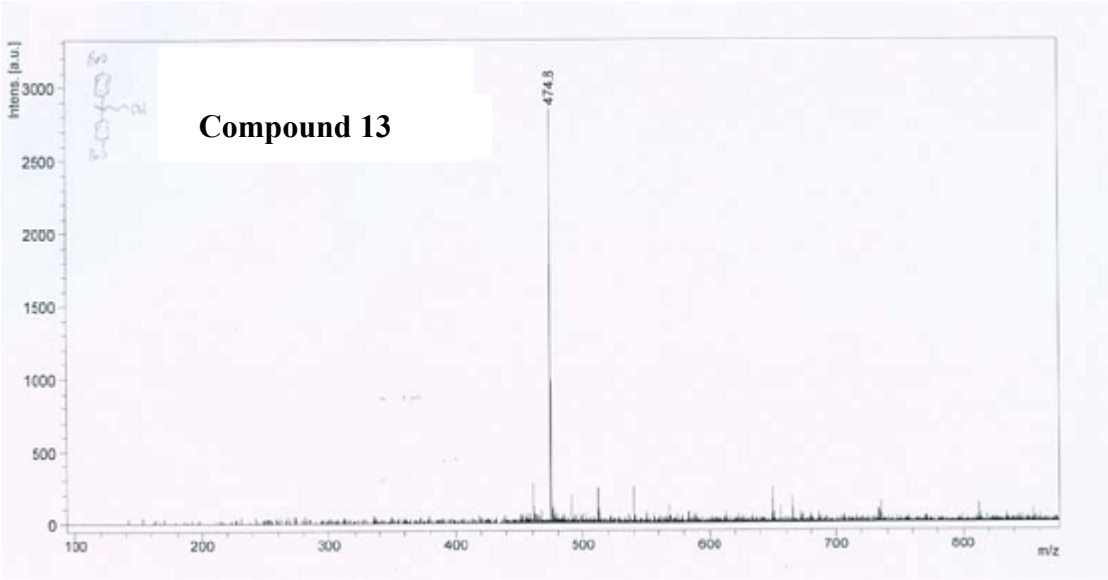

MALDI-TOF,CCA,11,2008,02,21
Compound 12
Intens. [a.u.]
4000
3000
2000
1000
0
502.8
518.8
200
400
600
800
1000
m/z

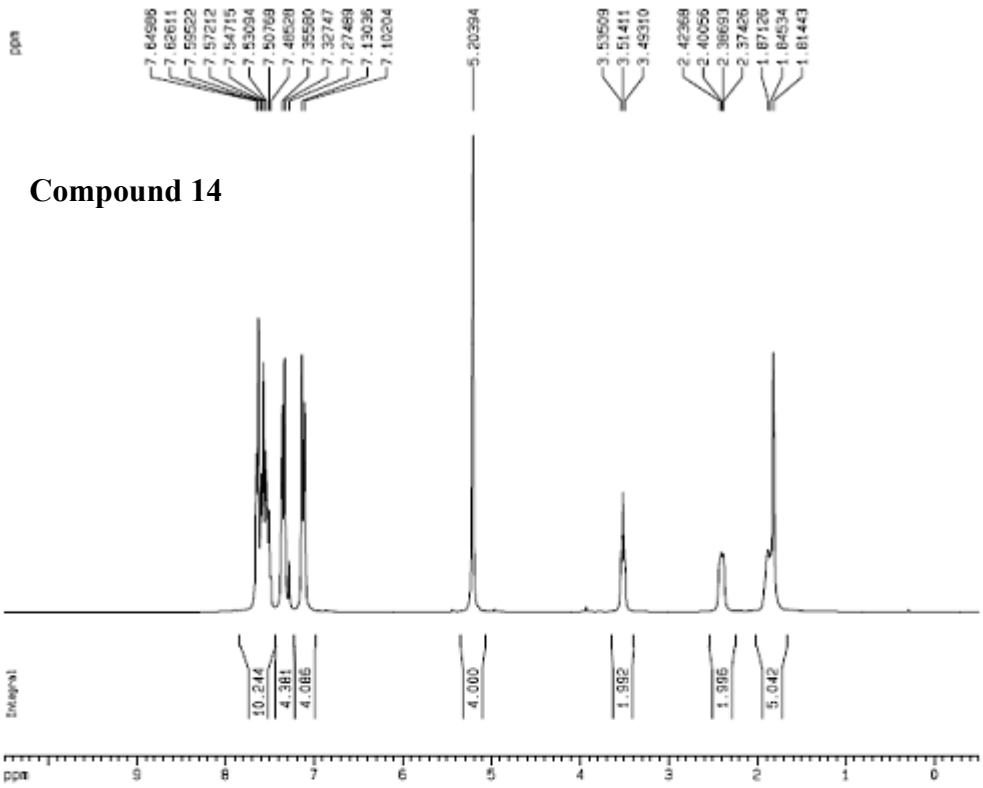

ppm
7.61970
7.59599
7.56575
7.54319
7.51803
7.50914
7.50334
7.49093
7.48035
7.46965
7.45711
7.35561
7.32651
7.27354
7.10818
7.07901
5.16342
3.71897
3.69796
3.67674
2.63495
2.32827
2.31379
2.30360
2.29947
2.27643
2.26598
1.80650
1.57616
1.54911
1.52804
Compound 13
Integral
10.191
4.000
4.023
3.985
1.982
1.011
2.012
2.996
2.133
ppm
8
6
4
2
0


ppm
156.906
142.473
137.412
128.814
128.571
128.171
127.786
114.452
77.976
77.751
77.550
77.125
70.172
63.366
44.977
36.359
29.450
26.227

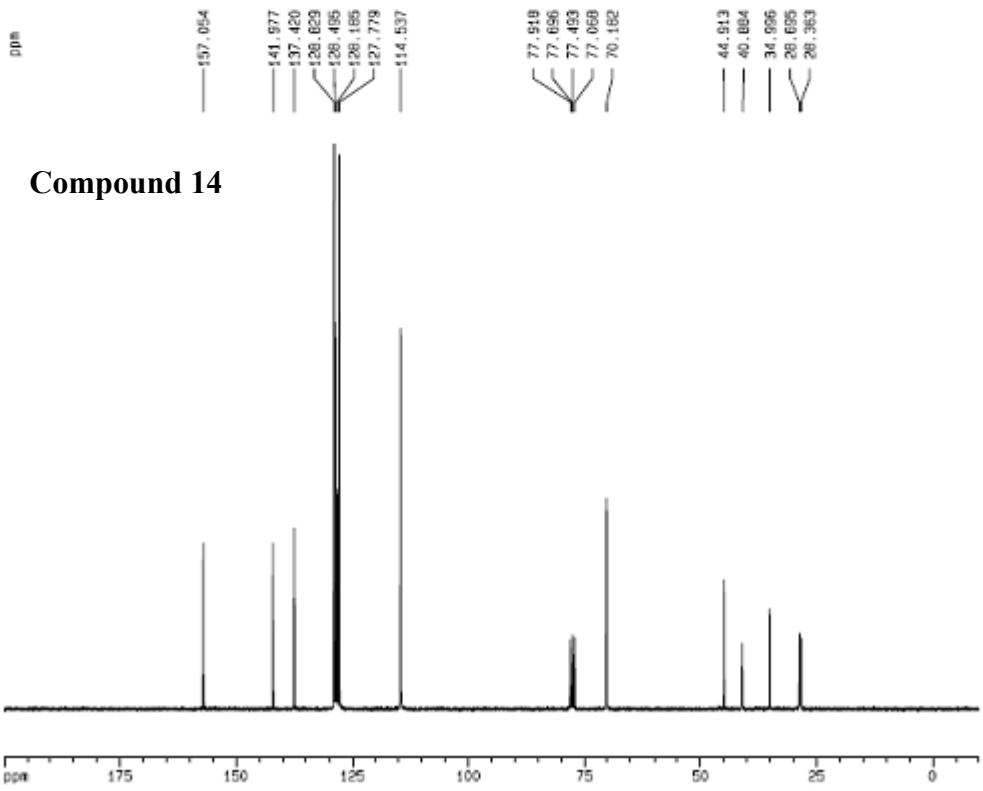
Compound 13


ppm
200
175
150
125
100
75
50
25
0

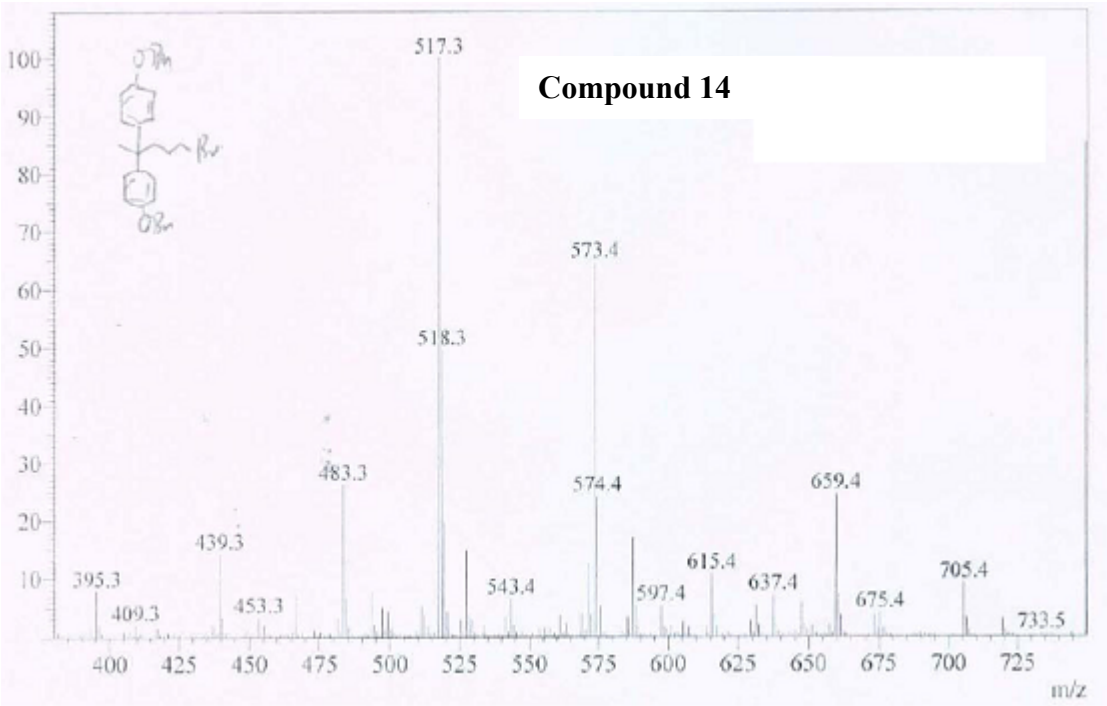

Compound 13
Intens. [a.u.]
3000
2500
2000
1500
1000
500
0
474.8
100
200
300
400
500
600
700
800
m/z

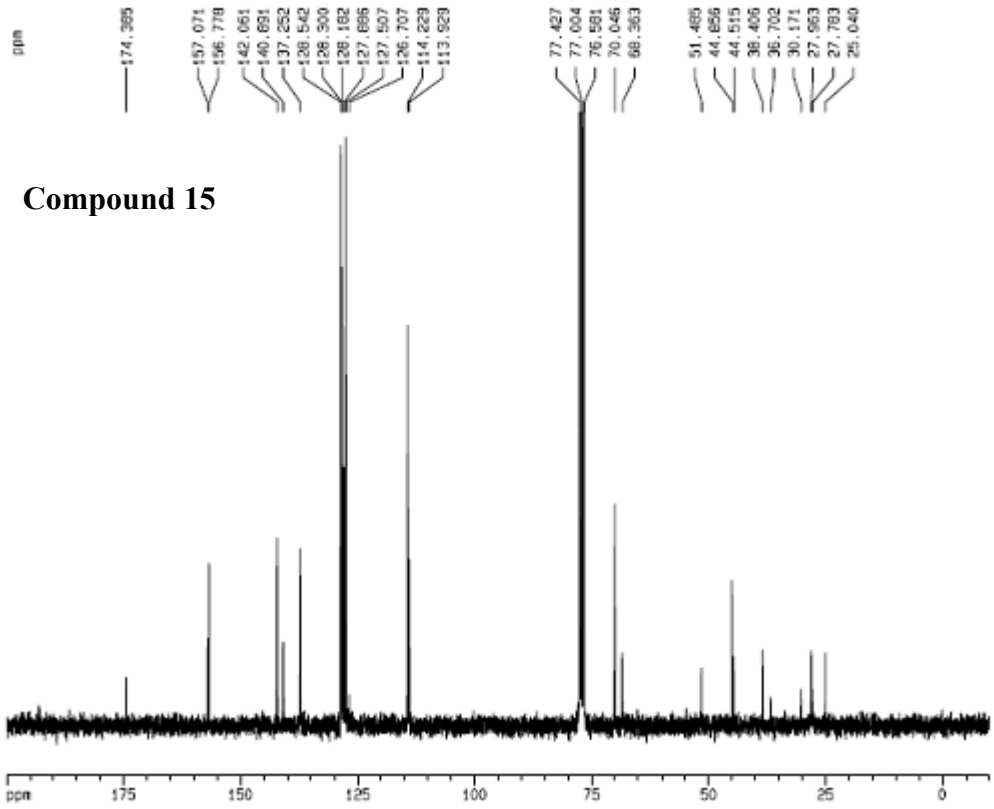


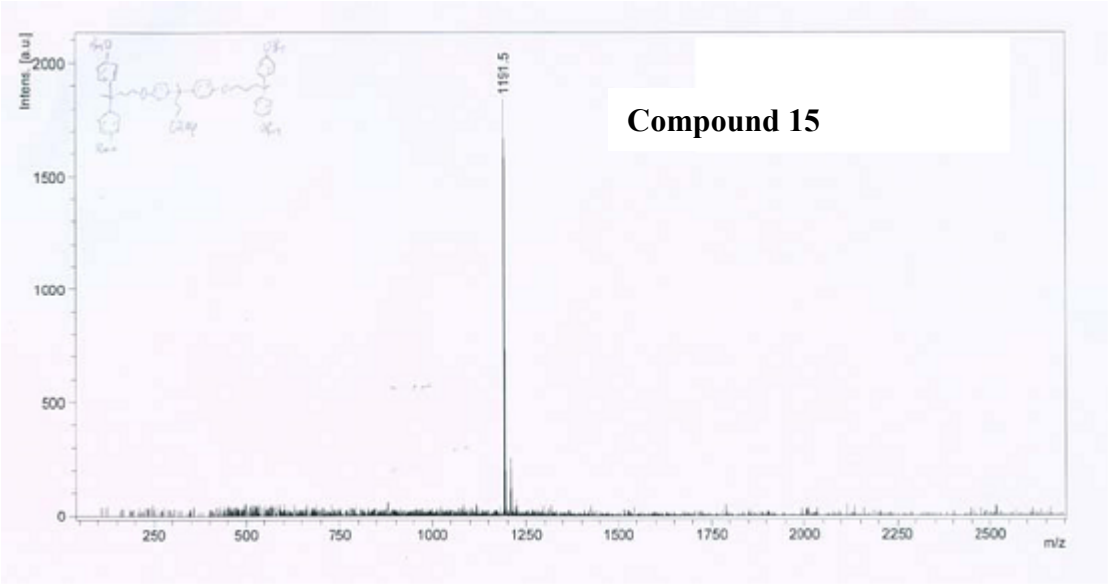
Compound 14



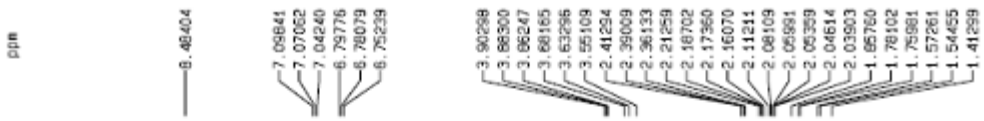
Compound 14


Compound 14
517.3
573.4
518.3
483.3
574.4
659.4
439.3
615.4
705.4
395.3
543.4
637.4
597.4
675.4
409.3
453.3
733.5
m/z

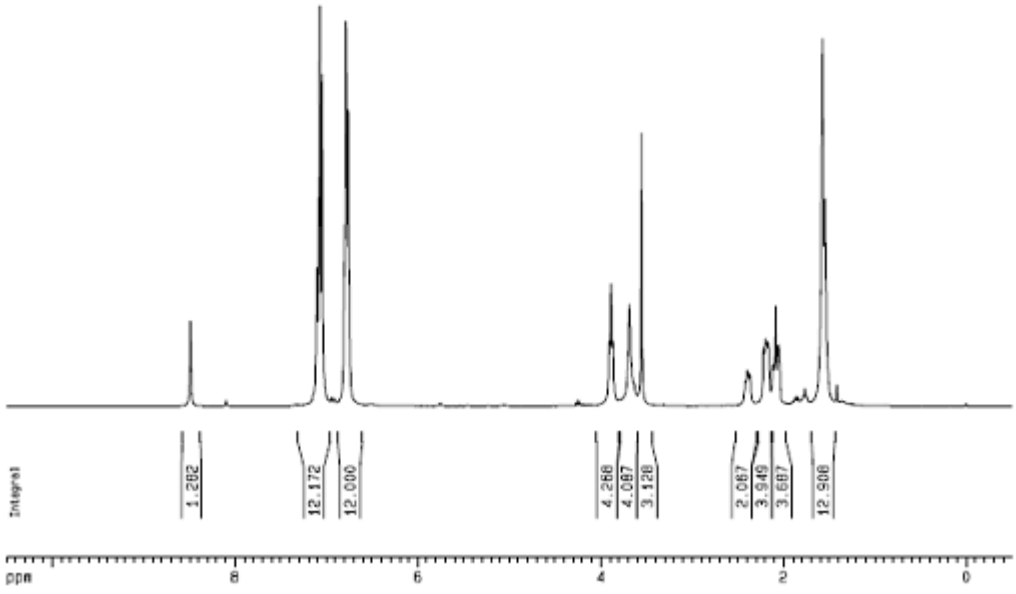

Compound 15
ppm

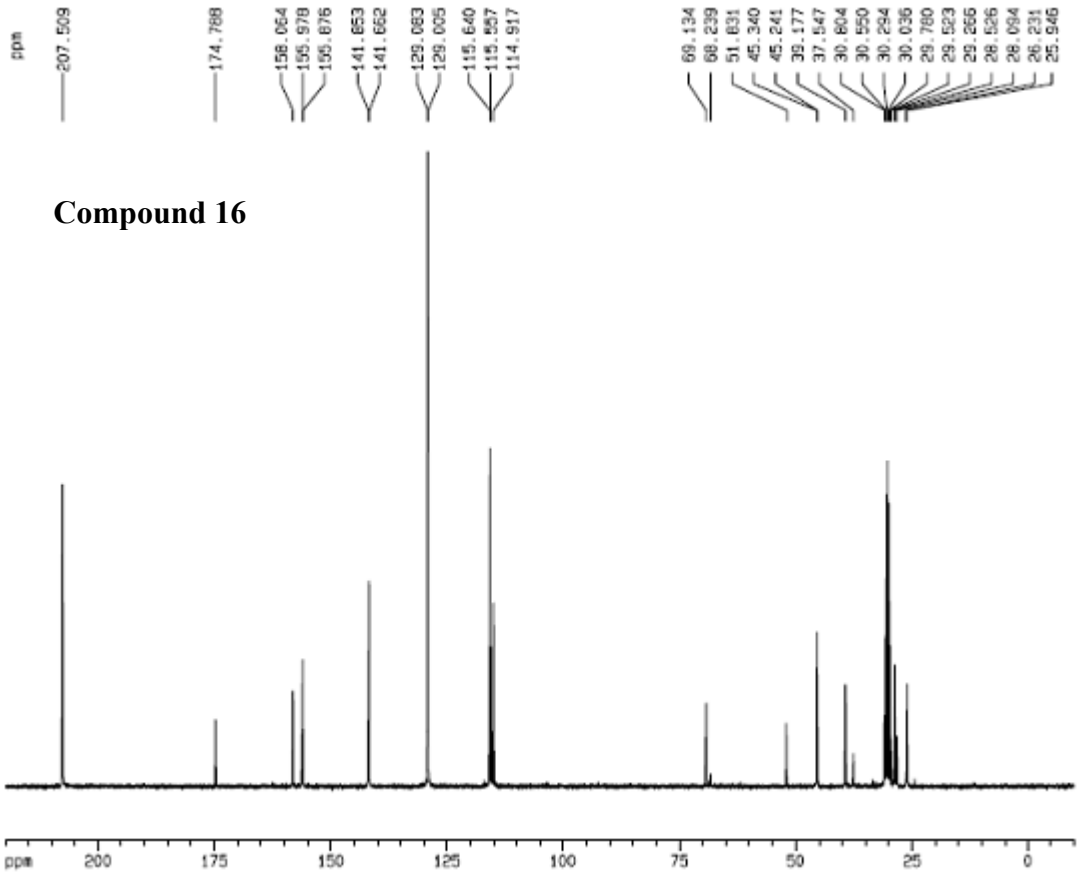


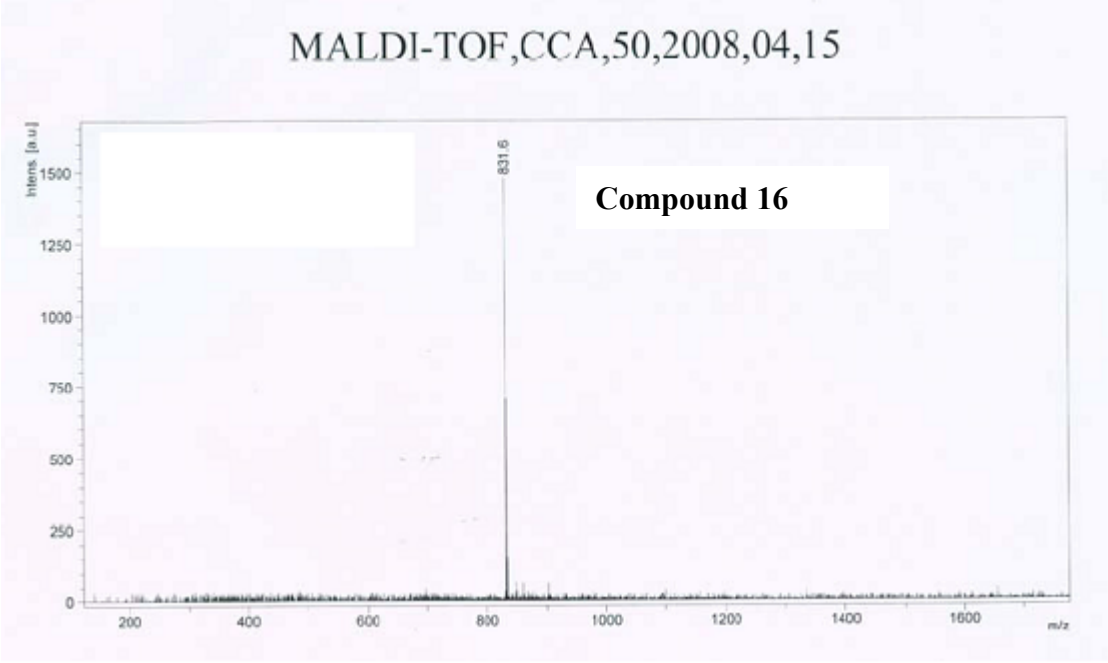
Compound 15

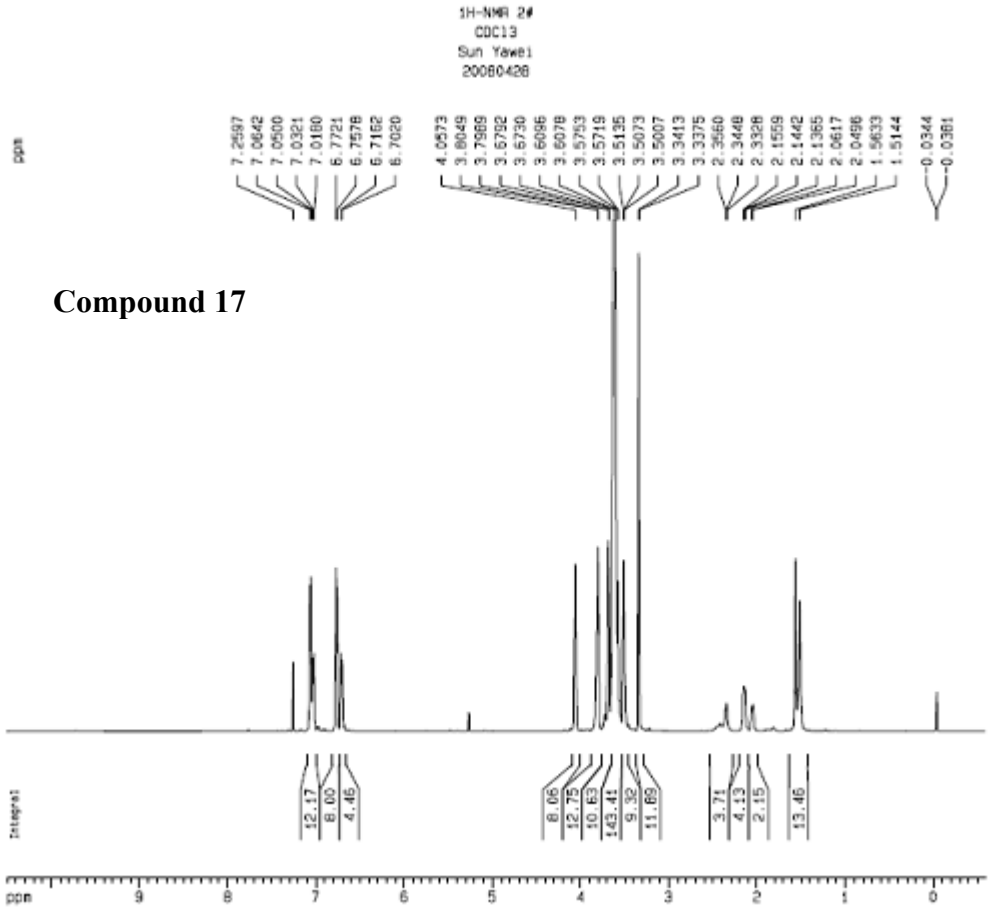


Compound 16

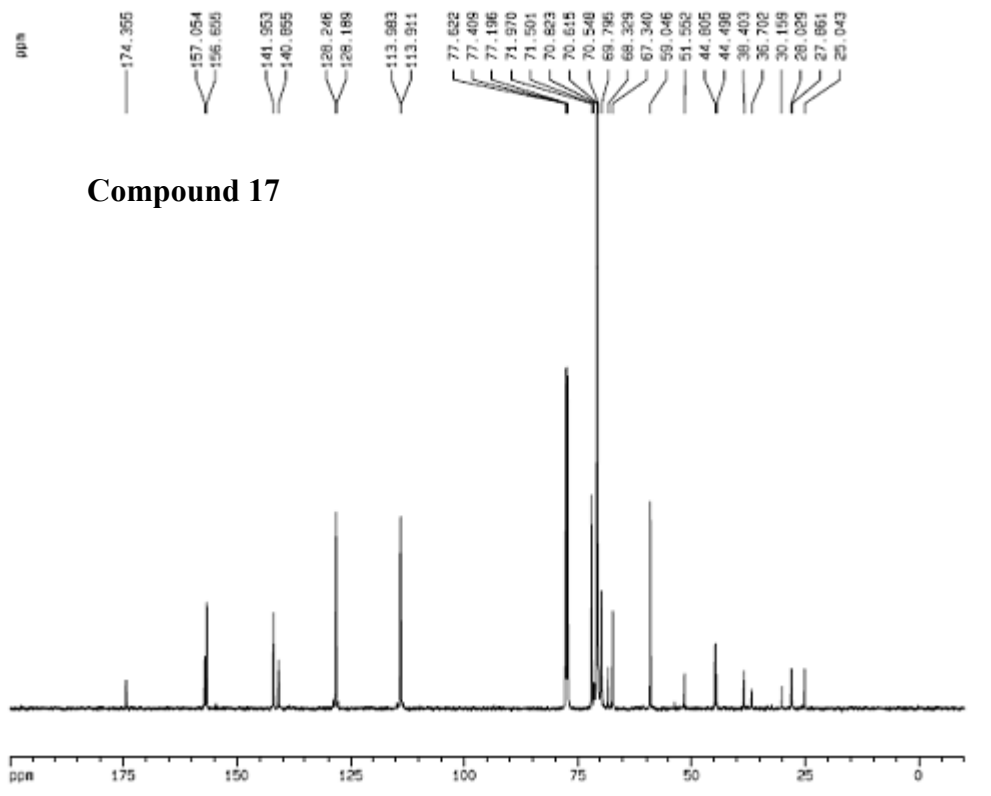



ppm
207.509
174.788
158.064
155.978
155.676
141.653
141.662
129.083
129.005
115.640
115.557
114.917
69.134
68.239
51.631
45.340
45.241
39.177
37.547
30.804
30.550
30.294
30.036
29.780
29.523
29.266
28.526
28.094
26.231
25.946
Compound 16
ppm
200
175
150
125
100
75
50
25
0

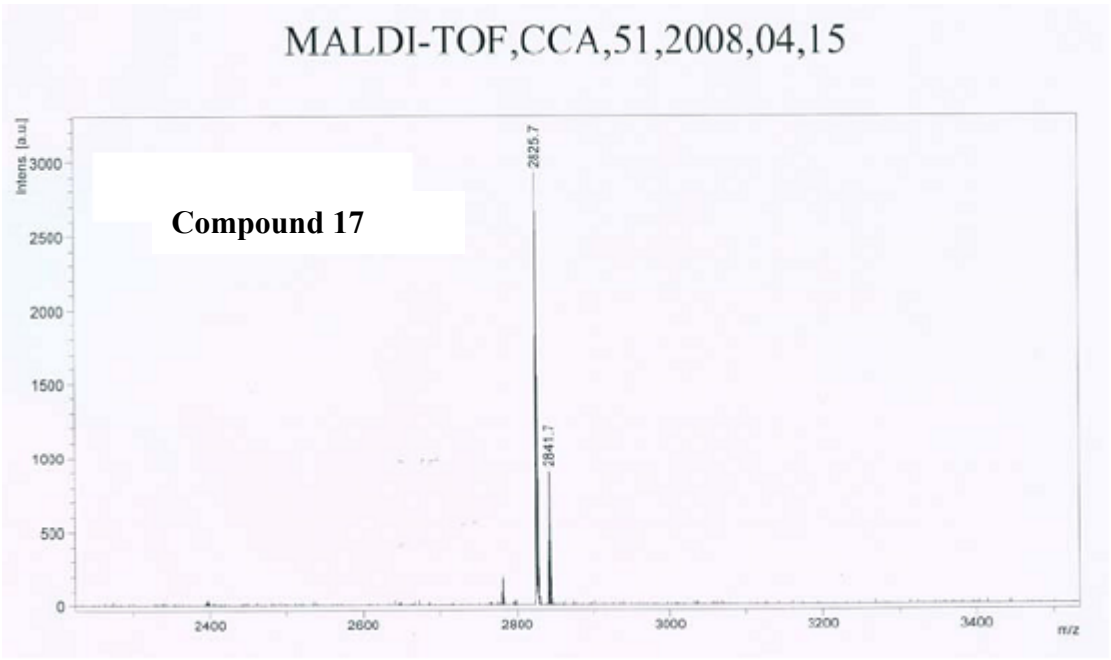

MALDI-TOF,CCA,50,2008,04,15
Intens. [a.u.]
1500
1250
1000
750
500
250
0
831.6
Compound 16
200
400
600
800
1000
1200
1400
1600
m/z

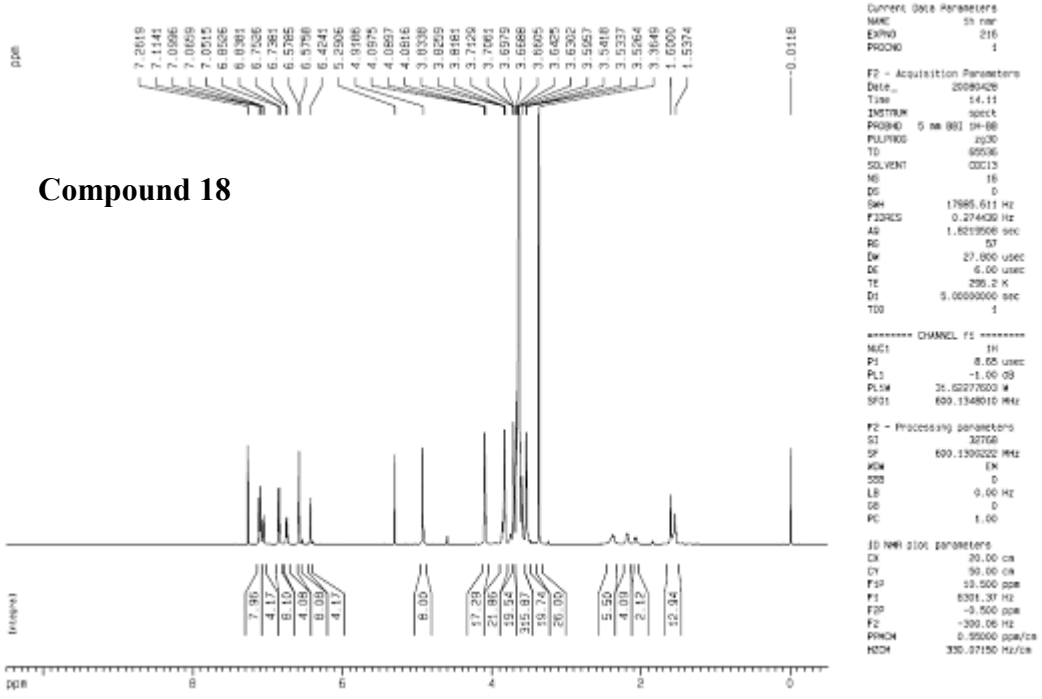


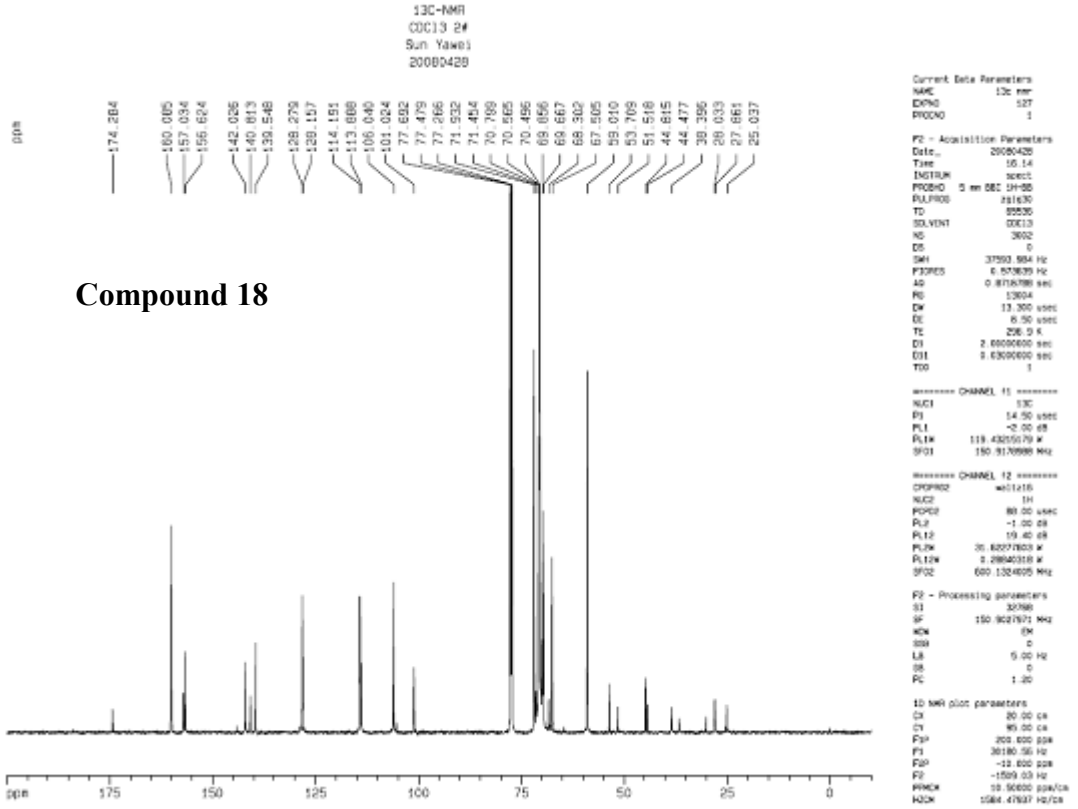
Compound 17

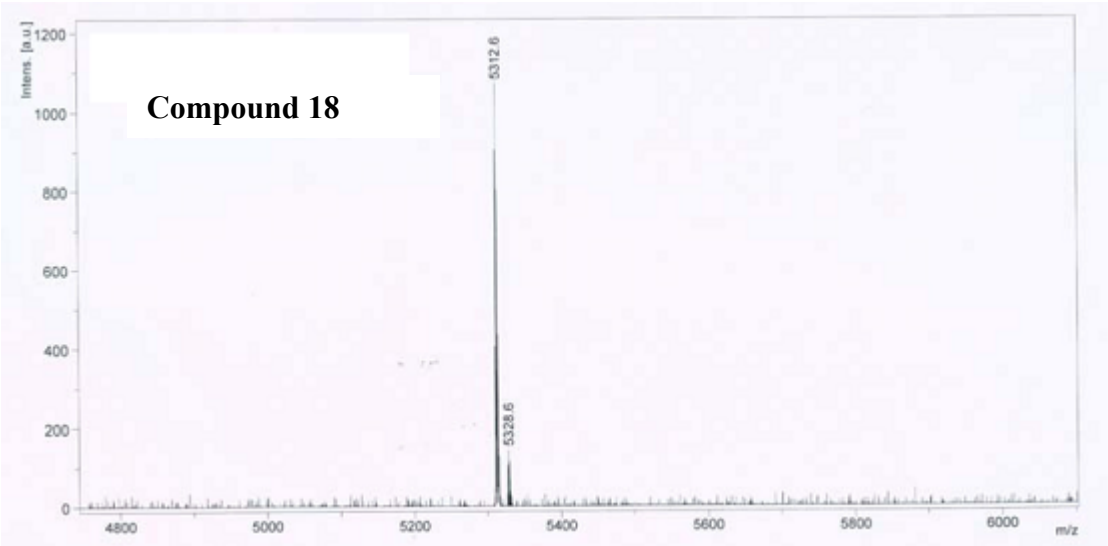


Compound 17

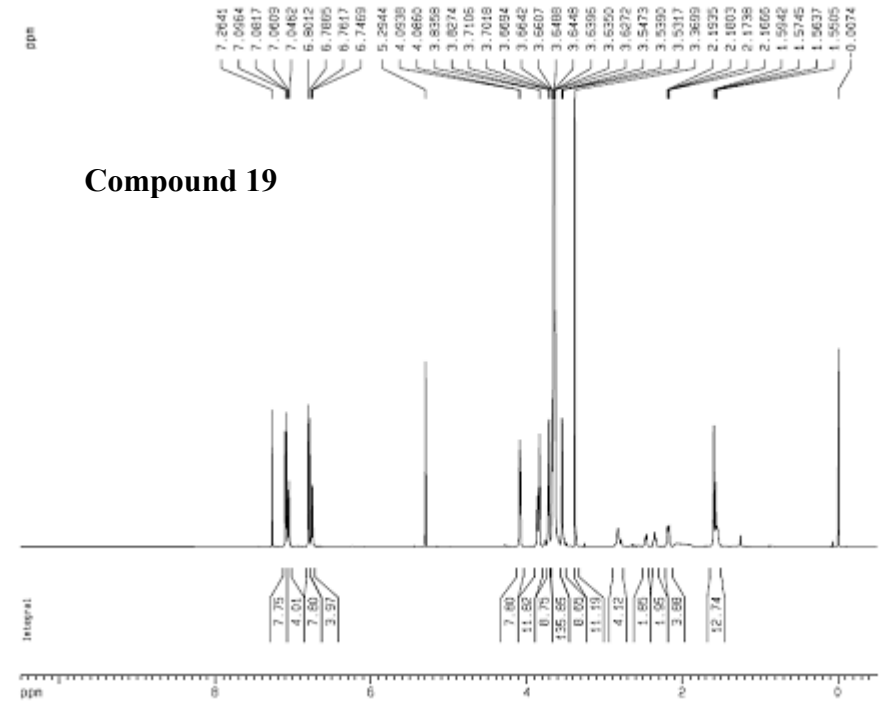

MALDI-TOF,CCA,51,2008,04,15
Compound 17
Intens [a.u.]
3000
2500
2000
1500
1000
500
0
2825.7
2841.7
2400
2600
2800
3000
3200
3400
m/z

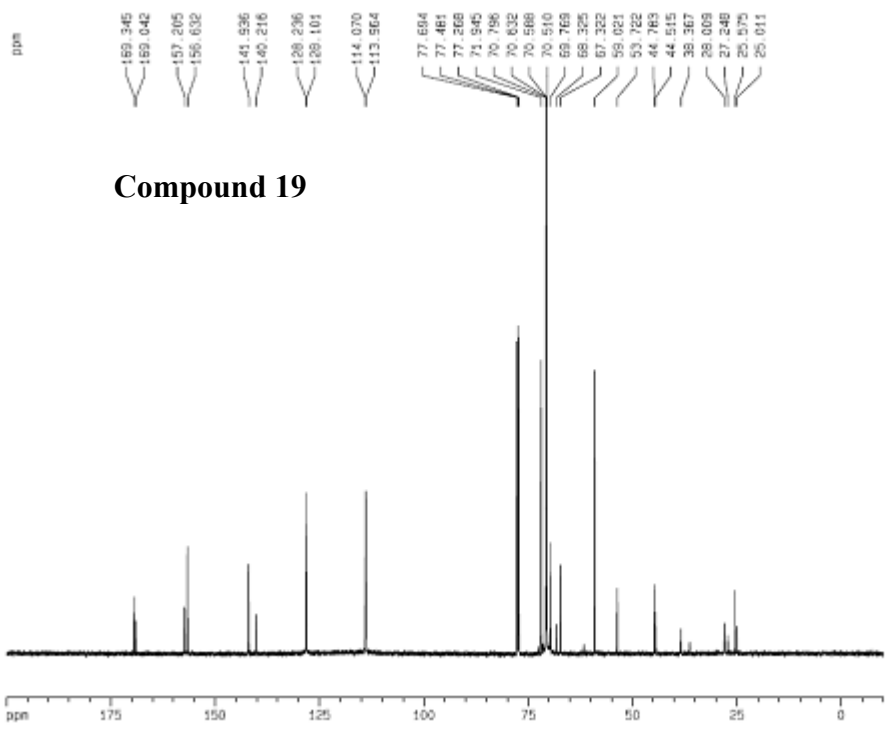

Compound 18
ppm
Integral
7.96
4.17
8.10
4.08
8.09
4.17
8.00
17.29
21.86
19.94
35.87
19.74
26.00
5.50
4.09
2.12
12.94


13C-NMR
CDCl3 2#
Sun Yawei
20080428
Compound 18
ppm
174.284
160.085
157.034
156.624
142.026
140.813
139.548
128.279
120.157
114.151
113.688
106.040
101.024
77.692
77.479
77.266
71.932
71.454
70.789
70.585
70.496
69.656
69.667
68.362
67.505
59.010
53.709
51.518
44.815
44.477
30.396
28.033
27.861
25.037
Current Data Parameters
NAME 13c mr
EXPNO 127
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080428
Time 16.14
INSTRUM spect
PROBHD 5 mm DUL 13C-H
PULPROG zgig30
TD 65536
SOLVENT CDCl3
NS 3602
DS 0
SWH 37593.984 Hz
FIDRES 0.573639 Hz
AQ 0.8716788 sec
RG 13004
DW 13.300 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 14.50 usec
PL1 +2.00 dB
PL1W 119.43205179 W
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 19.40 dB
PL2W 35.82277803 W
PL12W 0.28840318 W
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9027971 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.20
1D NMR plot parameters
CX 20.00 cm
CY 95.00 cm
F1P 200.000 ppm
F1 30180.56 Hz
F2P -10.000 ppm
F2 -1509.03 Hz
PPMCM 10.50000 ppm/cm
HZCM 1584.47637 Hz/cm
ppm
175
150
125
100
75
50
25
0

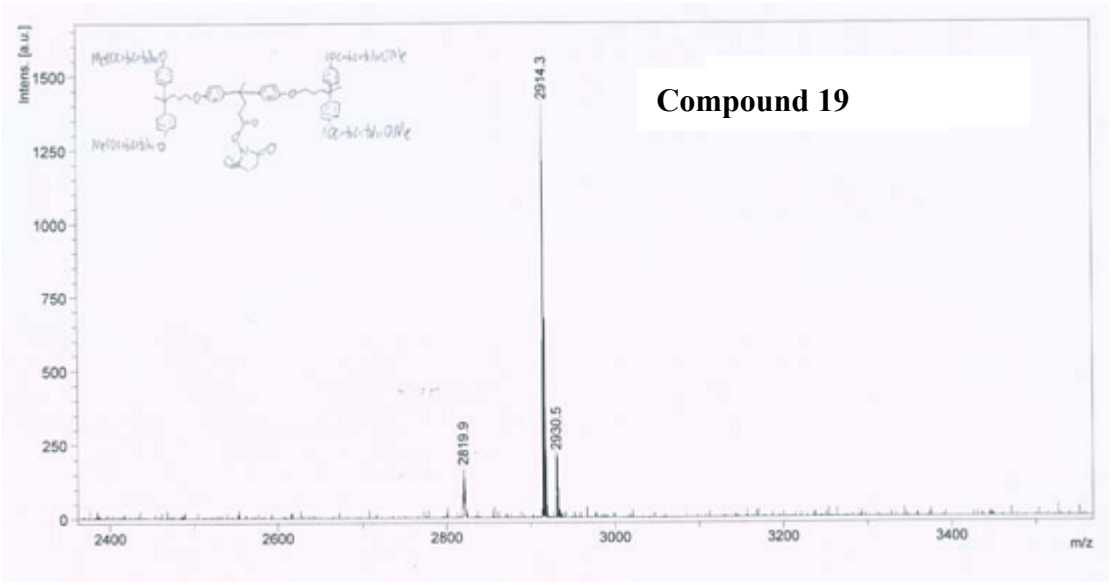

Compound 18
Intens. [a.u.]
1200
1000
800
600
400
200
0
5312.6
5328.6
4800
5000
5200
5400
5600
5800
6000
m/z

Compound 19

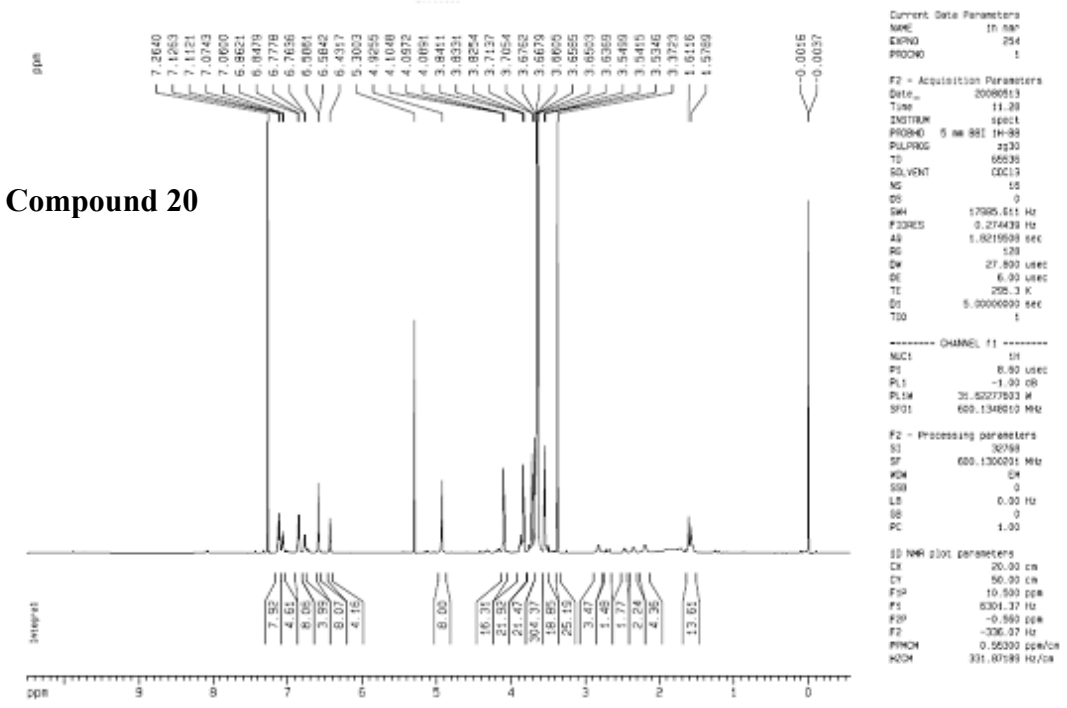




Compound 19



Compound 20



Current Data Parameters
NAME 1h nmr
EXPNO 254
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080513
Time 11.20
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219530 sec
RG 128
DW 27.800 usec
DE 6.00 usec
TE 295.3 K
D1 5.00000000 sec
TD0 1

-------- CHANNEL f1 --------
NUC1 1H
P1 8.90 usec
PL1 -1.00 dB
PL1W 35.52277832 W
SFO1 600.1348810 MHz

F2 - Processing parameters
SI 32768
SF 600.1300031 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 50.00 cm
F1P 10.500 ppm
F1 6301.37 Hz
F2P -0.500 ppm
F2 -336.07 Hz
PPMCM 0.55300 ppm/cm
HZCM 331.80188 Hz/cm