Supporting information for

Hydrogelation by Bile acid-Peptide Conjugates and *in situ* Synthesis of Silver and Gold Nanoparticles in Hydrogel Matrix

Mitasree Maity, Valiparambil Sanjayan Sajisha and Uday Maitra*

Department of Organic Chemistry, Indian Institute of Science, Bangalore- 560012, India

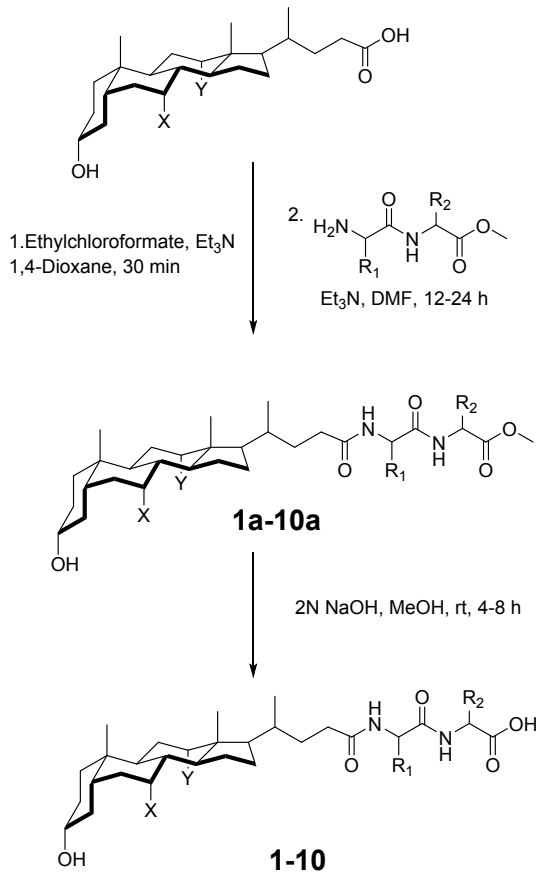
Email: maitra@orgchem.iisc.ernet.in

Contents

General considerations

All starting materials and solvents were obtained from commercial sources and were used without further purification. Distilled water was used for preparation of sodium phosphate buffer and NaOH for gelation study. Melting points of the product were determined on a Digimelt melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer at 400 MHz and 100 MHz, respectively. Scanning election micrographs were recorded on a SIRION instrument. Prior to the measurements the dried gels were coated with a thin gold layer. AFM imaging was carried out on a JPK NANO WIZARD II in non-contact mode. UV spectrums were recorded on Perkin Elmer. Transmission electron microscopy (TEM) was done on a JEM 2100F instrument. Samples were placed on a carbon-coated copper grid with subsequent drying and staining with uranyl acetate, followed by air and then vacuum drying.

General Synthetic scheme for the bile acid peptide conjugates



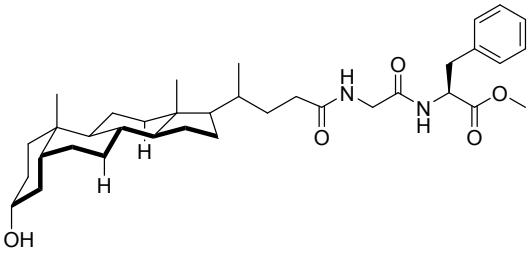
LC- Lithocholic acid (X=Y=H), DC- Deoxycholic acid (X=H, Y=OH), C- Cholic acid (X=Y=OH).

Bile acid-peptied conjugates synthesis

All reactions were carried out in oven dried glasswares. N-terminal of di-peptied (Boc-A_1-A_2-OMe, 0.2 mmol, 1 eq) was deprotected by trifluoroacetic acid (TFA, 0.8 mmol, 4 eq) in DCM stirring for 2 hour. Solvent was evaporated in high vacuum to get TFA salt. TFA salt was stirred with Et_3N (0.3 mmol, 1.5 eq) in DMF at room temperature for 30 min to get corresponding free amine. At the same time in another flask, bile acid (0.13 mmol, 0.67 eq) was dissolved in 1,4-Dioxane at 10 °C, then Et_3N (0.2 mmol, 1 eq) was added to it and followed by ethyl chloroformate (0.2 mmol, 1 eq) and stirred it at room temperature for 30 min to prepared mixed anhydride. Free amine-dipeptied methyl ester in DMF was directly added to the freshly prepared bile acid-anhydride. Stirring was continued for 12-24h and monitor by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate, was washed with water, and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel (100-200 mesh), using ethyl acetate/petroleum ether as the eluent. The hydrolysis of bile acid-dipeptide methyl ester conjugates were done with aqueous NaOH in MeOH and progress of reactions were monitored by TLC. Methanol was removed under reduced pressure and the solution was acidified with 1 (N) hydrochloric acid until a precipitate was formed. The resulting suspension was filtered under vacuum. The pure product was obtained by column chromatography 100-200 mesh silica gel with MeOH/$CHCl_3$.

Data of compounds

LC-G-*L*F-OMe (1a)



Yield- 68%, white solid, Mp- 64-70 °C.

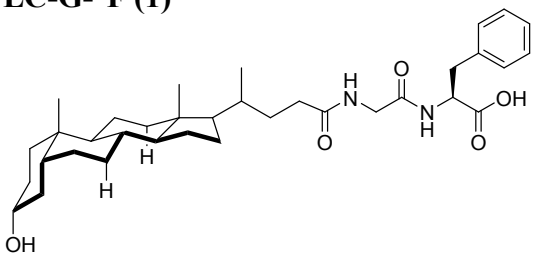
IR (KBr): 3302, 3066, 3029, 2934, 2864, 1748, 1659, 1652, 1538, 1446, 1376, 1214, 1177, 1110, 1068, 1032, 965, 945, 854, 813, 753, 701, 664, 605 cm^{-1}.

^1H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.28-7.22 (m, 3H), 7.11-7.09 (d, 2H, *J* = 8 Hz), 6.76-6.74 (m, 1H, NH), 6.40 (s, 1H, NH), 4.87-4.82 (m, 1H), 3.96-3.83 (dq, 2H, *J* = 16.8 Hz, 4 Hz), 3.72 (s, 3H), 3.64-3.58 (m, 1H), 3.17-3.04 (m, 2H), 2.31-0.96 (m, 29H, steroidal skeleton), 0.92-0.91 (m, 6H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 174.2, 171.7, 168.8, 135.7, 129.2, 128.6, 127.2, 71.9, 56.5, 56.0, 53.3, 52.5, 43.1, 42.8, 42.1, 40.5, 40.2, 37.9, 36.5, 35.9, 35.6, 35.4, 34.6, 33.3, 31.7, 30.6, 28.3, 27.2, 26.5, 24.3, 23.4, 20.9, 18.4, 12.1.

Mass Spec. (EI) m/z: M. Wt. calcd for $C_{36}H_{54}N_2O_5Na$ - 617.39; observed - 617.3931 (M+Na).

LC-G-^{L}F (1)



Yield- 90%, white solid, Mp- 110-125 °C.

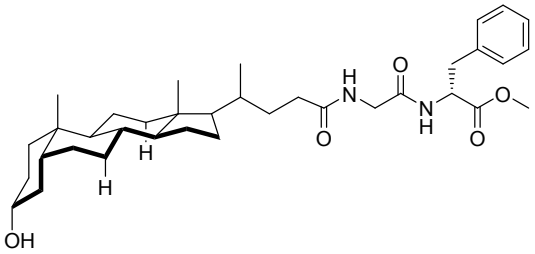
IR (KBr): 3322, 3062, 3029, 2936, 2865, 2519, 1731, 1660, 1531, 1455, 1378, 1335, 1218, 1113, 1067, 1031, 1013, 965, 945, 829, 805, 755, 700, 665, 494 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- CD_3OD) δ: 7.29-7.21 (m, 5H), 4.69-4.66 (m, 1H), 3.88-3.76 (m, 2H), 3.58-3.50 (m, 1H), 3.22-3.17 (m, 1H), 3.04-2.99 (dd, 1H, *J* = 16, 8 Hz), 2.33-0.96 (m, 29H, steroidal skeleton protons), 0.95 (s, 6H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, Solvent- CD_3OD) δ: 177.1, 171.3, 138.1, 130.4, 129.25, 127.8, 79.5, 72.4, 57.9, 57.4, 54.9, 43.9, 43.5, 43.3, 41.9, 41.9, 41.5, 38.4, 37.2, 37.1, 36.8, 36.5, 35.7, 33.8, 33.0, 31.2, 29.2, 28.3, 27.6, 25.3, 23.9, 21.9, 18.9, 12.5.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{35}H_{52}N_2O_5Na$ – 603.37; observed – 603.3774 (M+Na).

LC-G-^{D}F-OMe (2a)



Yield- 91%, white solid, Mp- 66-74 °C.

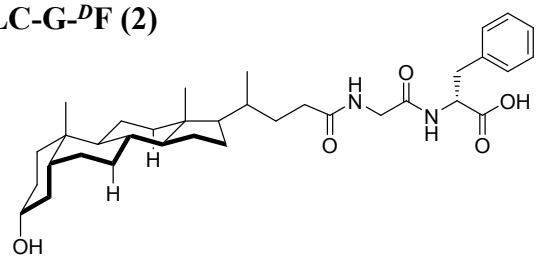
IR (KBr): 3271, 2925, 2860, 1742, 1645, 1528, 1443, 1375, 1212, 1032, 743 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.29-7.24 (m, 3H), 7.10-7.08 (d, 2H, *J* = 8 Hz), 6.55-6.53 (d, 1H, *J* = 7.2 Hz, NH), 6.24-6.23 (d, 1H, *J* = 4 Hz, NH), 4.88-4.83 (m, 1H), 3.94-3.85 (m, 2H), 3.73 (s, 3H), 3.65-3.59 (m, 1H, C_3-H), 3.17-3.05 (m, 2H), 2.31-0.986 (m, 29H, steroidal skeleton protons), 0.91 (m, 6H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 174.1, 171.5, 168.6, 135.5, 129.1, 128.5, 127.1, 71.7, 56.4, 55.9, 53.1, 52.3, 42.9, 42.6, 42.0, 40.3, 40.1, 37.7, 36.3, 35.7, 35.4, 35.2, 34.5, 33.1, 31.5, 30.4, 28.1, 27.1, 26.3, 24.1, 23.3, 20.7, 18.3, 11.9.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{36}H_{54}N_2O_5Na$ - 617.3930; observed - 617.3931 (M + Na).

LC-G-^{D}F (2)



Yield- 95%, white solid, Mp- 209-215 °C.

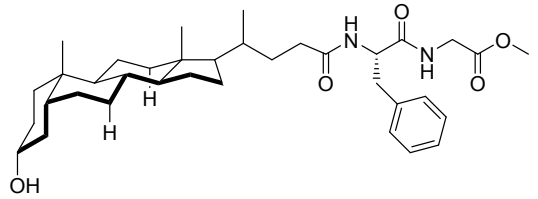
IR (KBr): 3481, 3400, 3028, 2936, 2866, 2520, 1715, 1655, 1629, 1537, 1516, 1446, 1381, 1368, 1344, 1305, 1280, 1246, 1223, 1186, 1125, 1106, 1068, 1035, 1012, 946, 861, 801, 739, 701, 617 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- DMSO-d_6) δ: 8.05 (d, 1H, *J* = 7.6 Hz), 7.95 (t, 1H, *J* = Hz), 7.25-7.18 (m, 5H), 4.43-4.38 (m, 2H), 3.70-3.56 (m, 2H), 3.05-3.00 (m, 1H, C_3-H), 2.89-2.83 (m, 1H), 2.18-1.10 (m, steroid back bone protons), 0.86 (s, 6H), 0.59 (s, 3H).

^{13}C NMR (100 MHz, Solvent- DMSO-d_6) δ: 173.2, 173.1, 169.3, 137.8, 129.5, 128.5, 126.8, 70.2, 56.4, 55.9, 53.7, 42.6, 42.0, 41.9, 37.2, 36.6, 35.7, 35.3, 34.6, 32.4, 31.7, 30.7, 28.1, 27.2, 26.5, 24.2, 23.6, 20.8, 18.6, 12.2.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{35}H_{52}N_2O_5Na$ - 603.37; observed - 603.3773 (M + Na).

LC-^{L}F-G-OMe (3a)



Yield- 95%, white solid, Mp- 83-86 °C.

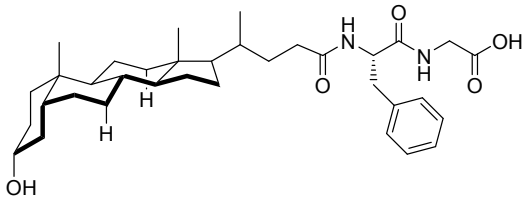
IR (KBr): 3400, 3294, 2936, 2865, 1756, 1654, 1545, 1445, 1371, 1207, 1181, 1068, 1034 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.29-7.20 (m, 5H), 6.62 (s, 1H), 6.20-6.18 (d, 1H, *J* = 8 Hz), 4.76-4.70 (q, 1H, *J* = 8 Hz), 4.03-3.88 (dq, 2H, *J* = 17.6 Hz, 5.6 Hz), 3.73 (s, 3H), 3.65-3.59 (m, 1H), 3.13-3.04 (m, 2H), 2.25-0.96 (m, steroidal CH and CH_2 peak) 0.92 (s, 3H), 0.89-0.87 (d, 3H, *J* = 8 Hz), 0.65 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 173.8, 171.3, 169.7, 136.4, 129.2, 128.5, 126.9, 71.7, 56.4.55.8, 54.0, 52.2, 42.6, 42.0, 41.08, 40.3, 40.09, 37.9, 36.3, 35.7, 35.3, 34.5, 33.3, 31.5, 30.5, 28.1, 27.1, 26.3, 24.1, 23.3, 20.7, 18.2, 11.9.

Mass Spec.(EI) m/z: M. Wt. calcd. for $C_{36}H_{54}N_2O_5Na$ - 617.58; observed- 617.3930 (M + Na).

LC-^{L}F-G (3)



Yield - 86%, white solid, Mp- 115-117 °C.

IR (KBr): 3405, 2931, 2863, 1736, 1654, 1638, 1527, 1448, 1384, 1213, 1195, 1033 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- MeOH-d_4) δ: 7.9 (s, 1H), 7.29-7.20 (m, 5H), 4.70-4.66 (dd, 1H, *J* = 8 Hz, 4.8 Hz), 3.90 (s, 2H), 3.57-3.52 (m, 1H), 3.24-3.18 (dd, 1H, *J* = 14 Hz, 5.2 Hz) 2.90-2.84 (dd, 1H, *J* = 14 Hz, 10 Hz), 2.3-0.96 (m, steroidal CH and CH_2 peak), 0.95 (s, 3H), 0.91-0.89 (d, 3H, *J* = 8 Hz), 0.65 (s, 3H).

^{13}C NMR (100 MHz, Solvent- MeOH-d_4) δ: 175.2, 172.7, 137.2, 128.8, 127.9, 126.2, 78.0, 70.9, 56.4, 55.9, 54.2, 42.4, 40.6, 42.1, 40.6, 40.4, 40.0, 37.3, 35.8, 35.7, 35.3, 35.0, 34.2, 32.4, 31.6, 29.7, 27.7, 26.9, 26.2, 23.8, 22.5, 20.5, 17.4, 11.1.

Mass Spec.(EI) m/z: M. Wt. calcd. for $C_{35}H_{52}N_2O_5Na$ - 603.58; observed - 603.3776 (M+Na).

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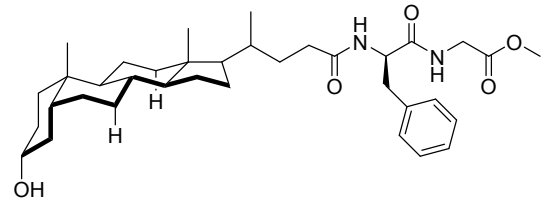
LC-^{D}F-G-OMe (4a)



Yield- 50%, white solid, Mp- 163.1-166.3 °C.

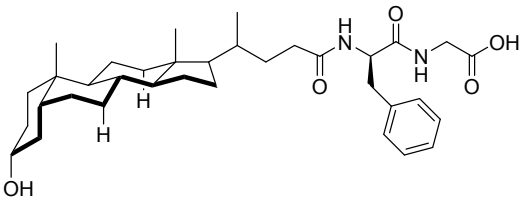
IR (KBr): 3329, 3290, 2930, 2860, 1759, 1654, 1545, 1445, 1371, 1207, 1181, 1068, 1024 cm^{-1}.

^{1}H NMR (400 MHz, Solvent- $CDCl_3$) δ: 7.29-7.20 (m, 5 H), 6.69 (s, 1H, NH), 6.26-6.24 (s, 1H, *J* = 8 Hz), 4.78-4.72 (q, 1H, *J* = 8 Hz), 4.03-3.89 (dq, 2H, *J* = 18.4 Hz, 4 Hz), 3.72 (s, 3H), 3.64-3.59 (m, 1H), 3.12-3.03 (m, 2H), 2.3-0.97 (m, steroid protons), 0.96 (s, 3H), 0.87-0.85 (d, 3H), 0.62 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 173.8, 171.5, 169.8, 136.6, 129.5, 128.8, 127.0, 71.9, 56.5, 56.0, 54.1, 52.4, 42.8, 42.2, 41.2, 40.5, 40.2, 38.1, 36.5, 35.9, 35.5,35.4, 34.6,33.4, 31.6, 30.6, 28.3, 27.3, 26.5, 24.2, 23.4, 20.9, 18.4, 12.1.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{36}H_{54}N_2O_5Na$- 617.40; observed – 617.3936 (M+Na).

LC-^{D}F-G (4)



Yield- 61%, white solid, Mp- 185-187 °C.

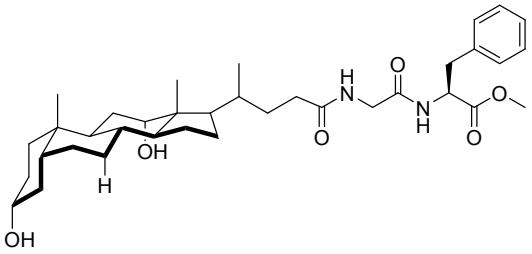
IR (KBr): 3400, 3028, 2936, 2866, 2525, 1715, 1657, 1629, 1539, 1526, 1446, 1381, 1368, 1344, 1305, 1280, 1246, 1223, 1186, 1125 cm^{-1}.

^{1}H NMR (400 MHz, Solvent- DMSO-d_6) δ: 8.23 (s, 1H), 8.03-8.01(d, 1H, *J* = 8 Hz), 7.24-7.16 (m, 5H), 4.52 (s, 1H), 3.75-3.74 (d, 2H, *J* = 4.8 Hz), 3.03-3.01 (m, 1H), 2.74-2.68 (m, 1H), 2.1-0.92 (m, steroid protons), 0.87 (s, 3H), 0.79-0.78 (d, 3H, *J* = 8 Hz), 0.55 (s, 3H).

^{13}C NMR (100 MHz, Solvent- DMSO-d_6) δ: 172.8, 172.1, 171.5, 138.5, 129.5, 128.3, 126.5, 70.3, 56.5, 56.1, 53.9, 48.9, 42.6, 41.9, 41.3, 37.9, 36.7, 35.8, 35.5, 35.1, 34.6, 32.6, 31.7, 30.8, 28.0, 27.3, 26.5, 24.2, 23.7, 20.8, 18.6, 12.3.

Mass Spec.(EI) m/z: M. Wt. cacld. for $C_{35}H_{52}N_2O_5Na$, 603.38; found 603.3776 (M+Na).

DC-G-^{L}F-OMe (5a)



Yield- 71%, white solid, Mp- 68-73 °C.

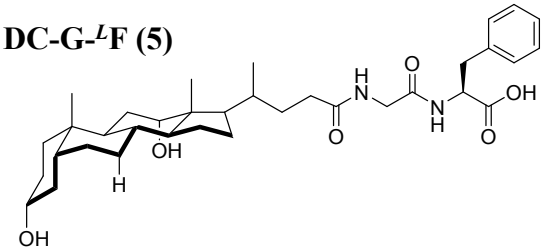
IR (KBr): 3408, 3064, 3030, 2937, 2864, 1746, 1652, 1539, 1447, 1417, 1377, 1337, 1216, 1178, 1112, 1089, 1065, 1043, 968, 943, 922, 851, 814, 755, 701 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.29-7.24 (m, 3H), 7.11-7.09 (d, 2H, *J* = 8 Hz), 6.74-6.62 (d, 1H, *J* = 8 Hz), 6.51-6.49 (t, 1H, *J* = 4.8 Hz), 4.87-4.81 (q, 1H, *J* = 8 Hz), 3.97 (s, 1H), 3.92-3.89 (m, 1H), 3.72 (s, 3H), 3.63-3.57 (m, 1H), 3.16-3.04 (dq, 2H, *J*= 14 Hz, 5.6 Hz), 2.35-2.10 (m, 4H), 1.90-0.99 (m, steroid skeletal protons), 0.99-0.97 (d, 1H, *J* = 8 Hz), 0.91 (s, 3H, Me), 0.67 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 174.2, 171.7, 168.8, 135.6, 129.1, 128.6, 127.2, 73.1, 71.8, 53.2, 52.4, 48.1, 46.9, 46.4, 42.9, 42.0, 37.7, 36.3, 35.9, 35.3, 35.2, 34.1, 33.5, 33.0, 31.4, 30.4, 28.6, 27.5, 27.1, 26.1, 23.7, 17.5, 12.8.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{36}H_{54}N_2O_6Na$ - 633.3880; Observed - 633.3885 (M+Na).

DC-G-^{L}F (5)



Yield- 70%, white amorphous solid.

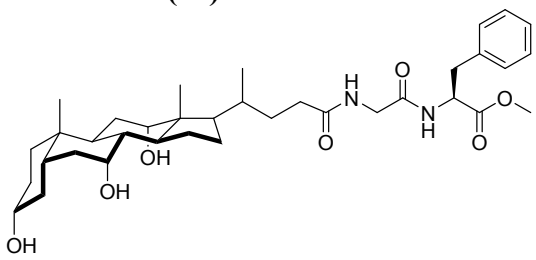
IR (KBr): 3404, 2937, 2864, 1734, 1718, 1654, 1534, 1448, 1384, 1217, 1115, 1089, 1064, 1041, 1014, 968, 944, 914, 851, 757, 700 cm^{-1}.

^1H MNR (400 MHz, Solvent- MeOH-d_4) δ: 7.26-7.19 (m, 5H), 4.64 (brs, 2H), 3.95 (s, 1H), 3.88-3.71 (m, 2H), 3.52-3.42 (m, 1H), 3.21-3.16 (m, 1H), 3.04-2.99 (m, 1H), 2.33-2.27 (m, 1H), 2.16-2.10 (m, 2H), 1.90-1.03 (m, steroid skeletal protons), 1.01 (d, 1H, *J* = 6 Hz, Me), 0.93 (s, 3H, Me), 0.70 (s, 3H, Me).

^{13}C MNR (100 MHz, Solvent- MeOH-d_4) δ: 177.2, 171.3, 138.2, 130.4, 129.4, 127.7, 79.4, 74.0, 72.5, 48.0, 47.5, 43.6, 43.4, 38.5, 37.4, 37.2, 36.8, 36.4, 35.3, 34.8, 33.8, 32.9, 31.0, 29.9, 28.6, 28.4, 27.4, 24.8, 23.6, 17.7, 13.1.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{35}H_{52}N_2O_6Na$ – 619.4; observed- 619.3737 (M+Na).

C-G-^{L}F-OMe (6a)



Yield- 61%, white solid, Mp- 84-95 °C.

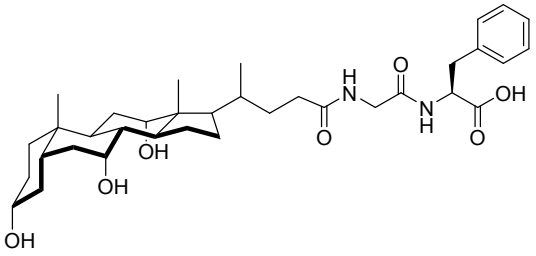
IR (KBr): 3409, 3065, 3029, 2933, 2866, 1743, 1654, 1542, 1534, 1457, 1447, 1438, 1376, 1339, 1216, 1117, 1077, 1043, 980, 950, 914, 900, 857, 812, 753, 701 cm^{-1}.

^1H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.29-7.10 (m, 5H), 4.84-4.78 (q, 1H, *J* = 8 Hz), 3.94 (s, 1H), 3.90-3.86 (m, 2H), 3.82 (s, 1H), 3.69 (s, 3H), 3.39-3.37 (m, 1H), 3.15-2.99 (m, 2H), 2.31-2.10 (m, 4H), 1.99-0.96 (m, steroid skeletal protons), 0.98 (d, 3H, *J* = 6.4 Hz), 0.88 (s, 3H), 0.66 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 175.3, 171.9, 169.5, 135.9, 129.3, 128.6, 127.1, 73.2, 71.9, 68.5, 53.4, 52.5, 46.5, 46.2, 43.3, 41.6, 39.8, 39.5, 37.9, 35.5, 34.9, 34.6, 32.5, 31.5, 30.3, 28.1, 27.7, 26.2, 23.4, 22.5, 17.5, 12.4.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{36}H_{54}N_2O_7Na$ - 649.38; Observed - 649.3826 (M+Na).

C-G-^{L}F (6)



Yield- 94%, white solid, Mp- 147-154 °C.

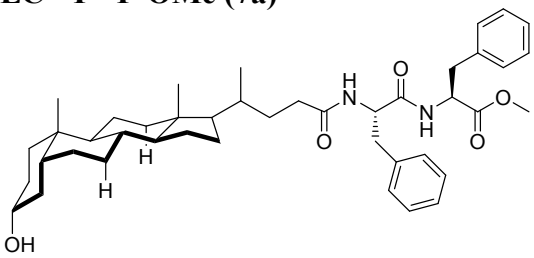
IR (KBr): 3264, 2929, 1798, 1637, 1542, 1448, 1295, 1164, 1022 cm^{-1}.

^1H MNR (400 MHz, Solvent- MeOH-d_4) δ: 7.29-7.19 (m, 5H), 4.69-4.65 (m, 2H), 3.95 (s, 1H), 3.88- 3.77 (m, 3H), 3.40-3.36 (m, 1H), 3.21-3.17 (dd, 1H, *J* = 16 Hz, 5.2 Hz), 3.04-2.99 (m, 1H), 2.34-1.08 (m, steroid skeletal protons), 1.03-1.01 (d, 3H, *J* = 8 Hz), 0.92 (s, 3H), 0.71 (s, 3H).

^{13}C MNR (100 MHz, Solvent- MeOH-d_4) δ: 175.8, 173.0, 169.9, 136.5, 128.8, 127.9, 126.3, 77.91, 72.5, 71.3, 67.6, 67.3, 53.4, 45.9, 41.8, 41.6, 41.4, 39.4, 36.8, 35.3, 34.9, 34.3, 34.2, 32.3, 31.4, 29.9, 27.1, 26.3, 22.7, 21.6, 16.2, 11.4.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{35}H_{52}N_2O_7Na$ - 635.37; observed - 635.3672 (M+Na).

LC-^{L}F-^{L}F-OMe (7a)



Yield- 89%, white amorphous solid.

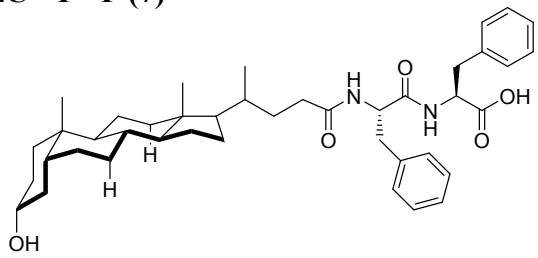
IR (KBr): 3414, 2928, 2861, 2098, 1751, 1654, 1545, 1444, 1364, 1213, 1176, 1031, 749 cm^{-1}.

^1H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.26-7.17 (m, 8H), 7.02-7.00 (d, 2H, *J* = 8 Hz), 6.54-6.52 (d, 1H, *J* = 8 Hz), 6.24-6.22 (d, 1H, *J* = 8 Hz), 4.76-4.65 (m, 2H), 3.64 (s, 3H), 3.62-3.58 (m, 1H), 3.03-3.01 (m, 4H), 2.3-0.98 (m, steroid skeletal protons), 0.91-0.87 (m, 6H), 0.61 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 173.4, 171.2, 170.5, 136.4, 135.5, 129.3, 129.1, 128.6, 128.5, 127.1, 126.9, 71.8, 56.4, 55.9, 53.9, 53.3, 52.3, 42.7, 42.0, 40.3, 40.1, 38.0, 37.8, 36.4, 35.4, 35.3, 34.5, 33.3, 31.5, 30.5, 28.2, 27.1, 26.3, 24.1, 23.3, 20.7, 18.3, 11.9.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{43}H_{60}N_2O_5Na$ – 707.4; observed – 707.4401 (M+Na).

LC-^{L}F-^{L}F (7)



Yield- 88%, white solid, Mp- 120-130 °C.

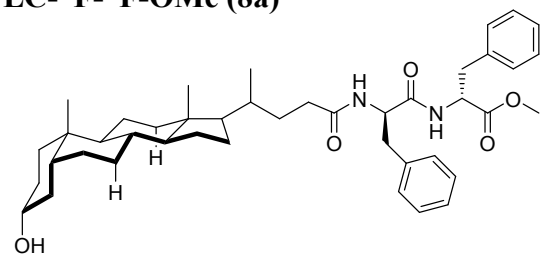
IR (KBr): 3298, 2925, 2860, 1642, 1526, 1449, 1216, 1030, 739 cm^{-1}.

^1H MNR (400 MHz, Solvent- MeOH-d_4) δ: 7.28-7.09 (m, 10H), 4.64-4.63 (m, 2H), 3.57-3.51 (m, 1H), 3.23-2.94 (m, 3H), 2.83-2.66 (m, 1H), 2.14-0.93 (m, steroid skeletal protons), 0.94 (s, 3H), 0.89-0.87 (d, 3H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, Solvent- MeOH-d_4) δ: 175.1, 172.1, 171.8, 137.1, 136.7, 129.0, 128.8, 128.0, 127.96, 127.9, 126.4, 126.3, 126.2, 78.0, 70.9, 56.4, 55.9, 54.2, 54.1, 53.7, 42.4, 42.1, 40.4, 40.0, 37.3, 36.9, 35.75, 35.7, 35.3, 35.0, 34.2, 32.4, 31.6, 29.7, 27.7, 26.9, 26.2, 23.8, 22.5, 20.5, 17.4, 11.1.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{42}H_{58}N_2O_5Na$ - 693.43; Observed - 693.4243 (M+Na).

LC-*D*F-*D*F-OMe (8a)



Yield- 74%, white amorphous solid.

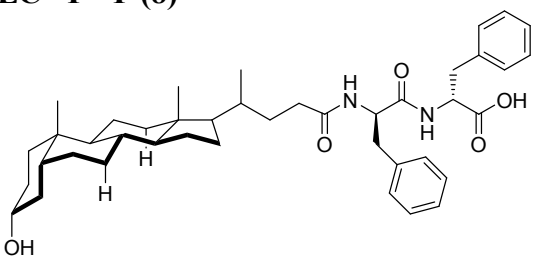
IR (KBr): 3424, 2929, 2861, 2090, 1749, 1655, 1545, 1444, 1364, 1213, 1171, 1031, 749 cm^{-1}.

^1H MNR (400 MHz, $CDCl_3$) δ: 7.24-7.17 (m, 8 H), 7.02-7.00 (d, 2H, *J* = 8 Hz), 6.51-6.49 (d, 1H, *J* = 8 Hz), 6.21-6.19 (d, 1H, *J* = 8 Hz), 4.76-4.64 (m, 2H), 3.67 (s, 3H), 3.62-3.58 (m, 1H), 3.09-2.93 (m, 4H), 2.21-0.95 (m, steroid skeletal protons), 0.91 (s, 3H), 0.87-0.85 (d, 3H), 0.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 171.2, 170.6, 136.4, 135.6, 129.3, 129.1, 128.49, 128.48, 127.0, 126.9, 71.7, 60.3, 56.4, 55.9, 53.9, 53.3, 52.2, 42.6, 42.0, 40.3, 40.1, 38.0, 37.8, 36.4, 35.7, 35.4, 35.3, 34.5, 33.3, 31.5, 30.5, 28.2, 27.1, 26.3, 24.1, 23.3, 20.9, 20.7, 18.3, 14.1, 12.0.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{43}H_{60}N_2O_5Na$ - 707.45; observed - 707.4402 (M+Na).

LC-*D*F-*D*F (8)



Yield- 76%, white amorphous solid.

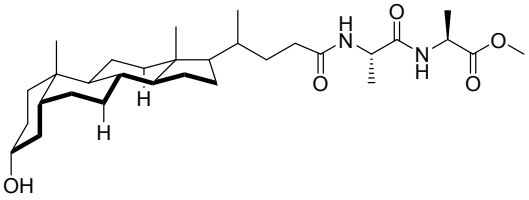
IR (KBr): 3299, 2925, 2860, 1645, 1527, 1449, 1216, 1032, 738 cm^{-1}.

^1H MNR (400 MHz, DMSO-d_6) δ: 8.13-8.11 (d, 1H, *J* = 8 Hz), 7.96-7.94 (d, 1H, *J* = 8 Hz), 7.28-7.08 (m, 10H), 4.53-4.38 (m, 2H), 3.10-3.05 (m, 1H), 2.99-2.92 (m, 2H), 2.70-2.64 (m, 1H), 2.1-0.9 (m, steroidal proton), 0.87 (s, 3H), 0.77-0.75 (d, 3H), 0.55 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.7, 172.3, 171.3, 133.0, 137.5, 129.3, 129.2, 129.1, 128.1, 128.0, 127.8, 127.7, 126.3, 126.1, 79.1, 69.8, 56.0, 55.6, 53.6, 42.2, 41.5, 37.3, 36.7, 36.3, 35.3, 34.7, 34.2, 32.1, 31.3, 30.3, 27.6, 26.8, 26.1, 23.8, 23.2, 18.1, 11.8.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{42}H_{58}N_2O_5Na$ - 693.43; Observed - 693.4243 (M+Na).

LC-^{L}A-^{L}A-OMe (9a)



Yield- 75%, white amorphous solid.

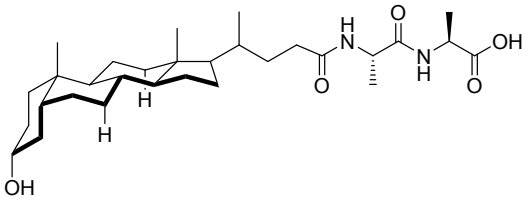
IR (KBr): 3436, 2971, 2870, 2839, 1772, 1644, 1540, 1280, 1207, 1037, 753 cm^{-1}.

^1H MNR (400 MHz, Solvent- $CDCl_3$) δ: 7.04-7.02 (d, 1H, *J*= 8 Hz), 6.38-6.36 (d, 1H, *J* = 8 Hz), 4.61-4.49 (m, 2H), 3.74 (s, 3H), 3.66-3.58 (m, 1H), 2.30-0.962 (m, steroidal peak and -Me group of Alanine), 0.91-0.90 (m, 6H), 0.63 (s, 3H).

^{13}C NMR (100 MHz, Solvent- $CDCl_3$) δ: 173.5, 173.1, 172.2, 71.8, 56.5, 56.0, 52.5, 48.5, 48.1, 42.7, 42.1, 40.4, 40.2, 36.5, 35.9, 35.5, 35.4, 34.6, 33.4, 31.7, 30.6, 29.7, 28.3, 27.2, 26.5, 24.2, 23.4, 20.9, 18.6, 18.4, 18.0, 12.1.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{31}H_{52}N_2O_5Na$ – 555.37; Observed – 555.37 (M+Na).

LC-^{L}A-^{L}A (9)



Yield- 94%, white solid, Melting point- 120-130 °C

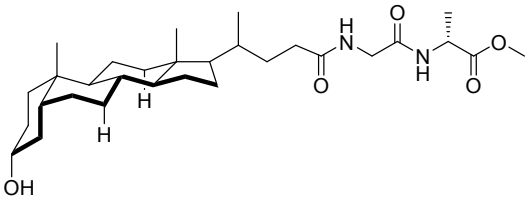
IR (KBr): 3796, 3463, 2937, 2924, 2863, 2852, 2880, 1732, 1634, 1538, 1453, 1384 cm^{-1}.

^1H MNR (400 MHz, Solvent: DMSO-d_6) δ: 8.05-8.03 (d, 1H, *J* = 8 Hz), 7.93-7.91 (d, 1H, *J* = 8 Hz), 4.31-4.24 (m, 1H), 4.17-4.10 (m, 1H), 3.16 (s, 1H), 2.16-0.91 (m, steroidal peak and Me group of Alanine), 0.87-0.86 (m, 6H), 0.59 (s, 3H).

^{13}C NMR (100 MHz, Solvent- DMSO-d_6) δ: 174.4, 172.7, 172.5, 79.6, 70.3, 56.5, 55.9, 48.9, 48.0, 47.8, 42.6, 41.9, 36.7, 35.8, 35.5, 35.3, 34.6, 32.5, 31.8, 30.8, 29.4, 28.1, 27.3, 26.6, 24.2, 23.7, 20.8, 18.7, 18.5, 17.6, 12.2.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{30}H_{50}N_2O_5Na$ - 541.36; Observed - 541.3617 (M+Na).

LC-G-*D*A-OMe (10a)



Yield- 66%, white solid, Mp- 170-173 °C.

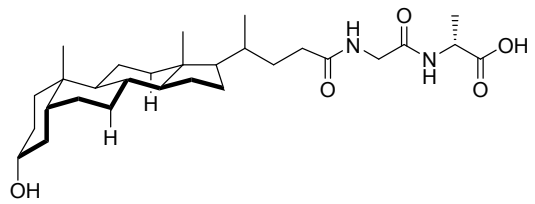
IR (KBr): 3796, 3463, 2937, 2924, 2863, 2852, 2880, 1732, 1634, 1538, 1453, 1384 cm^{-1}.

^1H MNR (400 MHz, Solvent- $CDCl_3$) δ: 6.67-6.65 (d, 1H, *J* = 8 Hz, NH), 6.28 (s, 1H), 4.61-4.54 (m, 1H), 4.02-3.91 (m, 2H), 3.76 (s, 3H), 3.66-3.57 (m, 1H), 2.31-0.96 (m,), 0.93-0.91 (m, 6H), 0.64 (s, 3H).

^{13}C NMR (100 MHz, Solvent: $CDCl_3$) δ: 174.2, 173.0, 168.6, 71.8, 56.4, 55.9, 52.5, 48.1, 43.0, 42.7, 42.0, 40.4, 40.1, 36.4, 35.8, 35.4, 35.3, 34.5, 33.2, 31.6, 30.5, 28.2, 27.1, 26.3, 24.1, 23.3, 20.7, 18.3, 18.1, 11.9.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{30}H_{50}N_2O_5Na$ - 541.36; Observed - 541.3618 (M+Na).

LC-G-*D*A (10)



Yield- 84%, white solid, Mp- 110-130 °C.

IR (KBr): 3796, 3463, 2937, 2924, 2863, 2852, 2880, 1732, 1634, 1538, 1453, 1384 cm^{-1}.

^{1}H MNR (400 MHz, Solvent- MeOH-d_4) δ: 4.45-4.39 (m, 1H), 3.94-3.82 (m, 2H), 3.57-3.51 (m, 1H), 2.39-0.99 (m, steroidal peak and Me group of Alanine), 0.99-0.96 (m, 6H), 0.70 (s, 3H, Me).

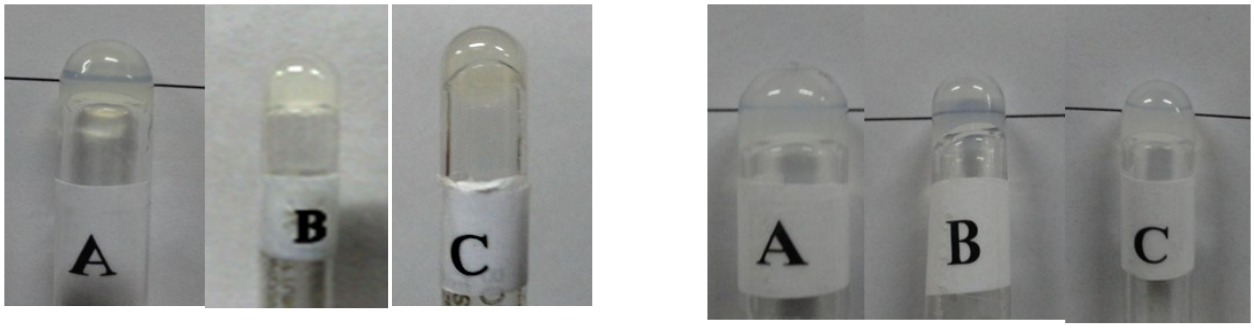
^{13}C NMR (100 MHz, Solvent- MeOH-d_4) δ: 175.7, 174.3, 169.8, 78.0, 70.9, 56.4, 55.9, 42.4, 42.07, 40.06, 35.8, 35.7, 35.4, 35.0, 34.2, 32.4, 31.5, 29.7, 27.8, 26.8, 26.2, 23.8, 22.5, 20.5, 17.4, 16.3, 11.0.

Mass Spec.(EI) m/z: M. Wt. calcd for $C_{29}H_{48}N_2O_5Na$ - 527.72; observed - 527.3461 (M+Na).

General procedures for gelation studies

Gelation tests for compounds **1-10** were done by weighing 3 mg of a particular compound in a test tube and adding 300 µL of the solvent in query. For checking gelation in presence of NaOH, 3 mg compounds were taken, 100 µL 0.5 N NaOH and followed by 200 µL distilled water was added. The obtained suspension was heated until it form a clear solution. The solution was allowed to reach room temperature or sonicated for 1 minute, after that gelations were checked by inverted test tube method.

Gel images of (1 wt%) LC-^{L}F-G (3) and LC-^{D}F-G (4)



LC-^{L}F-G (3) **LC-^{D}F-G (4)**

A= in NaOH, B= pH 8, C= pH 7

Single crystal X-ray analysis

Suitable crystal of **LC-G-^{L}F (1)** for single crystal analysis was grown from MeOH/ H_2O by slow evaporations.

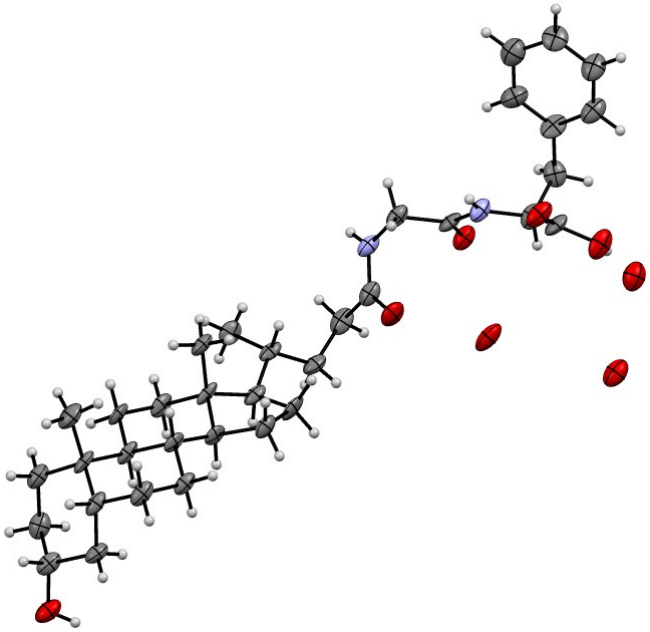


Figure S1: Single Crystal structure of **LC-G-^{L}F (1). 3 (O)**

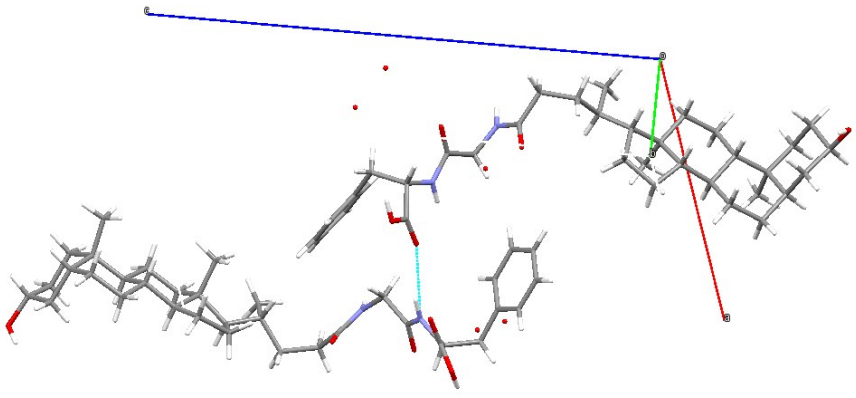


Figure S2: Packing structure of **LC-G-^{L}F (1). 3 (O)**

Table S1: Crystal data and structure refinement for mono.

Empirical formula	$C_{35}H_{52}N_2O_8$ [$C_{35}H_{52}N_2O_5$ + 3 (O)]
Formula weight	628.78
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.346(5)
b/Å	7.136(3)
c/Å	20.348(7)
α/°	90
β/°	105.843(17)
γ/°	90
Volume/Å^3	1724.7(11)
Z	2
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	0.085
F(000)	680.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.43 to 51.998
Index ranges	$-15 \leq h \leq 15$, $-8 \leq k \leq 5$, $-25 \leq l \leq 24$
Reflections collected	23601
Independent reflections	5181 [R_{int} = 0.1811, R_{sigma} = 0.1554]
Data/restraints/parameters	5181/1/411
Goodness-of-fit on F^2	0.993
Final R indexes [I>=2σ (I)]	R_1 = 0.0895, wR_2 = 0.2140
Final R indexes [all data]	R_1 = 0.1653, wR_2 = 0.2456
Largest diff. peak/hole / e Å^{-3}	0.43/-0.38
Flack parameter	1.1(10)

Experimental

Single crystals of $C_{35}H_{52}N_2O_8$ were LC-G-^{L}F (**1**), 3(O). A suitable crystal was selected and mounted on a **'Bruker APEX-II CCD'** diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [mono]

Crystal Data for $C_{35}H_{52}N_2O_8$ (M =628.78 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 12.346(5) Å, b = 7.136(3) Å, c = 20.348(7) Å, β = 105.843(17)°, V = 1724.7(11) Å^3, Z = 2, T = 100 K, μ(MoKα) = 0.085 mm^{-1}, *Dcalc* = 1.211 g/cm^3, 23601 reflections measured (3.43° ≤ 2Θ ≤ 51.998°), 5181 unique (R_{int} = 0.1811, R_{sigma} = 0.1554) which were used in all calculations. The final R_1 was 0.0895 (I > 2σ(I)) and wR_2 was 0.2456 (all data).

AgNPs and AuNPs synthesis in LC-G-$^{D/L}$F gel

It was found that increasing the concentration of the dopant (> 1 mM in 4.3 mM gel, 0.5 wt%) led to the agglomeration of small AuNPs/AgNPs to bigger clusters. Therefore, reduced doping (0.4 mM) of Au or Ag precursor in the hydrogel template was necessary for the smooth formation of silver/gold nanoparticles inside the gel fibres.

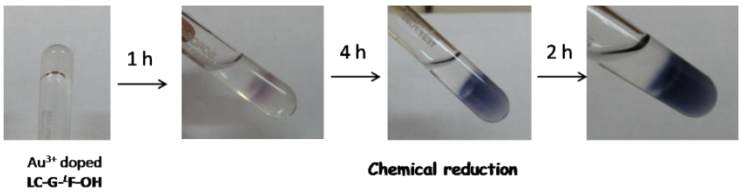


Figure S3: AuNPs synthesis in the hydrogel of **1** by chemical reduction of Au^{3+} (1.6 mM in 0.5 wt% gel).

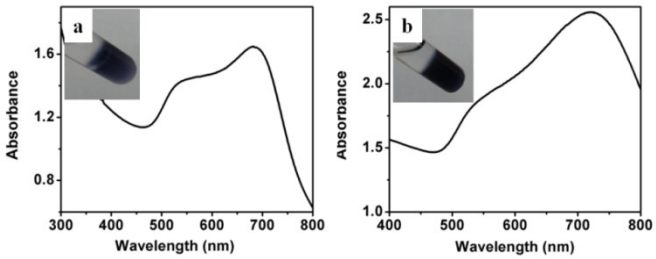


Figure S4: Absorption spectra of AuNPs formed in the hydrogels of (a) **1** and (b) **2** by chemical reduction of Au^{3+} (1.6 mM in 0.5 wt% gel).

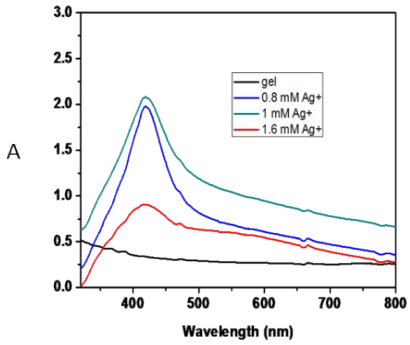


Figure S5: Absorption spectra of AgNPs formed in the hydrogel of **1** at different concentrations of Ag(I).

Nanoparticles formation were checked in pH 8 phosphate buffer gel for comparison as both gelator 1 and 2 formed gesl in pH 8, whereas gelator 2 did not form gel in pH 7.

We have checked effect of pH in case of LC-G-^{L}F (**1**). We have observed yellow AgNP formation (λ_{max} 420 nm) and pink color AuNP formation (λ_{max} 515 nm) using chemical reduction method in pH 7 which showed similar spectra as in pH 8. Also, at higher concentration of NaOH (pH 11), Ag^{+} salt produced precipitate of AgOH or Ag_2O, so we explored nanoparticle formation in pH 8.

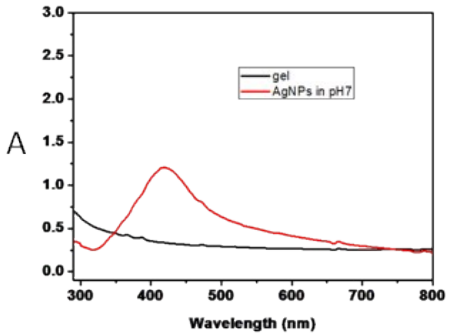


Figure S6: Absorption spectra of AgNPs formed in the hydrogel of **1** by chemical reduction of Ag^{+} (0.4 mM in 0.5 wt% gel).

Preparation of AgNPs by chemical reduction and photoreduction in LC-$^{D/L}$F-G gel

Silver nanoparticles were prepared in LC-^{L}F-G (**3**) and LC-^{D}F-G (**4**) hydrogel by the same procedure as followed for **1** and **2** (main text). For **3** a yellow colour and for **4** a brown colour appeared at the interface after 30 min. and after 12 h the entire gel turned yellow and brown, respectively (**Fig. S7**). The gels derived from compounds **3** and **4** showed absorbance peaks around 427 and 435 nm, respectively.

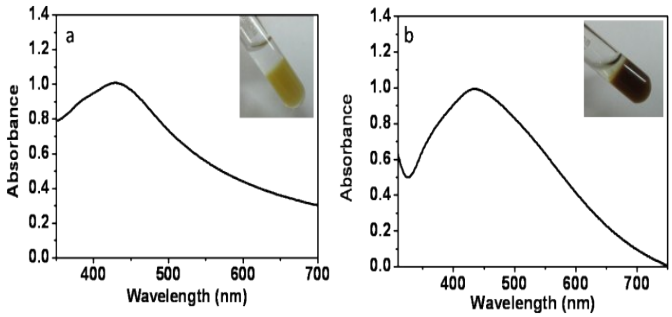


Figure S7: Absorption spectra of the AgNPs formed in the hydrogels of (a) **3** and (b) **4**

We have also examined photoreduction of Ag(I) in LC-^{D}F-G (**3**) and LC-^{L}F-G (**4**) gel by irradiating the gels by light from a 500 W tungsten lamp (Illuminance of the 500 watt tungsten bulb at a distance of 12 cm on a surface of 0.6 cm radius was 0.3 W measured using power meter). Silver doped gel **3** and **4** were turbid in nature. In case of LC-^{D}F-G (**3**) gel color changes from pink to brown.

Absorptions were recorded at regular time intervals and the data show the changes in the absorption spectrum.The pink gel showed peaks around 530 nm and with time 380 nm peaks appeared (**Fig. S8**).

Silver doped LC-^{L}F-G (**4**) gel was very turbid and after photo irradiation for 15 h, gel become little blackish color but in UV-Visible absorbance spectra there was no peak corresponding to Ag(0). Similar to LC-G-^{L}F (**2**) gel, dark brown colored appeared after addition of $NaBH_3CN$ to LC-^{L}F-G (**4**) gel.

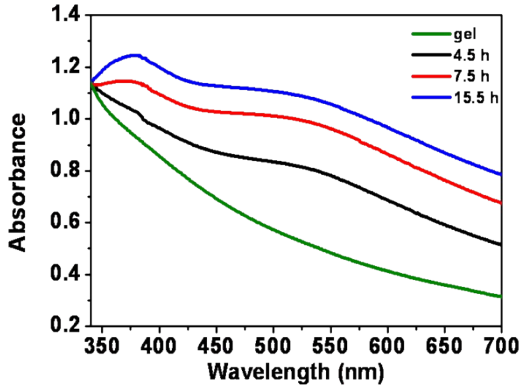


Figure S8: Absorption spectra as a function of irradiation time for AgNPs synthesized in LC-^{D}F-G (**4**) gel

FT-IR studies of LC-G-$^{D/L}$F xerogel and Ag(I) containing LC-G-$^{D/L}$F xerogel

FT-IR were recorded on Bruker putting solid xerogel directly to the sample holder. To verify the structural insight of Ag(I) dopped LC-G-$^{D/L}$F self assembled materials, FT-IR was used to study in xerogel states. In LC-G-^{D}F (**2**) xerogel show a strong C=O stretching peak at 1632 cm^{-1} and corresponding N-H bending and N-H stretching frequencies appearing at 1532 and 3456, 3283 cm^{-1} (**Table S2, Fig. S9**). Interestingly, in the Ag(I) containing (gelator/Ag+ ratio= 10.8) xerogel LC-G-^{D}F (**2**) of C=O stretching frequency at 1632 cm^{-1} shifted to 1652 cm^{-1}, whereas Ag(I) containing xerogel LC-G-^{L}F (**1**) no shift were observed. Infrared spectra of the xerogels indicated that Ag(I) coordinate strongly with the carbonyl group of the LC-G-^{D}F (**2**) than LC-G-^{L}F (**1**). Similar observation were made in different ratio of Ag(I) containing xerogel (**Table S3**, **Fig. S10**) also xerogel prepared in HEPES buffer (100 mM, pH 8).

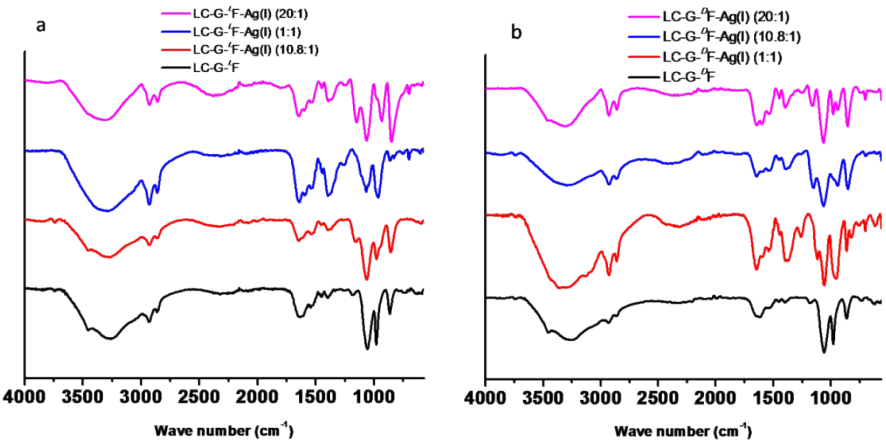


Figure S9: FT-IR spectra of LC-G-$^{L/D}$F (**1** and **2**) xerogel and silver(I) containing LC-G-$^{L/D}$F (**1** and **2**) xerogel in phosphate buffer

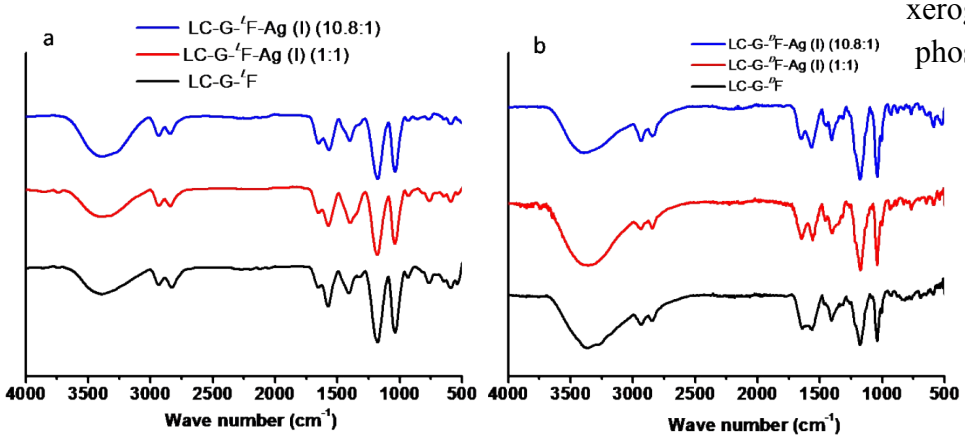


Figure S10: FT-IR spectra of LC- G-$^{L/D}$F (**1** and **2**) xerogel and silver(I) containing LC- G-$^{L/D}$F (**1** and **2**) xerogel in HEPES buffer

Table S2: FT-IR of LC-G-$^{D/L}$F xerogel and Ag(I) containing LC-G-$^{D/L}$F xerogel in Phosphate buffer (pH 8)

Samples	C=O stretching frequency (cm^{-1})	N-H bending frequency (cm^{-1})	C(O)-N stretching frequency (cm^{-1})	N-H stretching frequency (cm^{-1})
LC-G-^{L}F (**1**)	1642	1526	1396	3453, 3284
LC-G-^{L}F- Ag(I) (17.3:17.3 mM, gelator/Ag(I) ratio= 1)	1643	1595, 1536	1388	3334
LC-G-^{L}F- Ag(I) [17.3:1.6 mM, ratio= 10.8]	1648	1525	1391	3454, 3302
LC-G-^{L}F- Ag(I) (17.3:0.8 mM, ratio= 20.1)	1646	1599, 1534	1389	3325
LC-G-^{D}F (**2**)	1632	1532	1392	3456, 3283
LC-G-^{D}F- Ag(I) (17.3:17.3 mM, ratio= 1)	1647	1537	1397	3344
LC-G-^{D}F- Ag(I) (17.3:1.6 mM, ratio= 10.8)	1652	1593, 1526	1397	3332

LC-G-^{D}F- Ag(I) (17.3:0.8 mM, ratio= 20.1)	1645	1599, 1537	1397	3314

Table S3: FT-IR of LC-G-$^{D/L}$F xerogel and Ag(I) containing LC-G-$^{D/L}$F xerogel in HEPES buffer (pH 8)

Samples	C=O stretching frequency (cm^{-1})	N-H bending frequency (cm^{-1})	C(O)-N stretching frequency (cm^{-1})	N-H stretching frequency (cm^{-1})
LC-G-^{L}F (**1**)	1650	1577	1314	3376
LC-G-^{L}F- Ag(I) (17.3:17.3 mM, gelator/Ag(I) ratio= 1)	1650	1574	1327	3362
LC-G-^{L}F- Ag(I) [17.3:1.6 mM, gelator/Ag(I)= 10.8]	1655	1564	1314	3395
LC-G-^{D}F (**2**)	1639	1565	1319	3367
LC-G-^{D}F- Ag(I) (17.3:17.3 mM, ratio= 1)	1645	1558	1318	3368
LC-G-^{D}F- Ag(I) (17.3:1.6 mM, ratio= 10.8)	1649	1568	1317	3395

Note- Doping Ag(I) in LC-G-$^{D/L}$F gel in ratio of 1:1 in both buffer, some precipitate were formed which did not dissolved by heating, resulted turbid gel formation. This turbid gel was lyophilized and xerogel was used for FT-IR study.

Another interesting observation was in HEPES buffer, both the derivatives got reduced by photoreduction probably HEPES facilitated to reduce Ag (I).

Rheology studies of LC-G-$^{D/L}$F gel in pH 8

Rheological measurements at pH 8 showed gel behaviour as G' (Storage modulus) was always higher than G" (loss modulus). Rheological experiments indicated that both ^{L}F and ^{D}F derivate exhibited "soft" gel like behaviour.

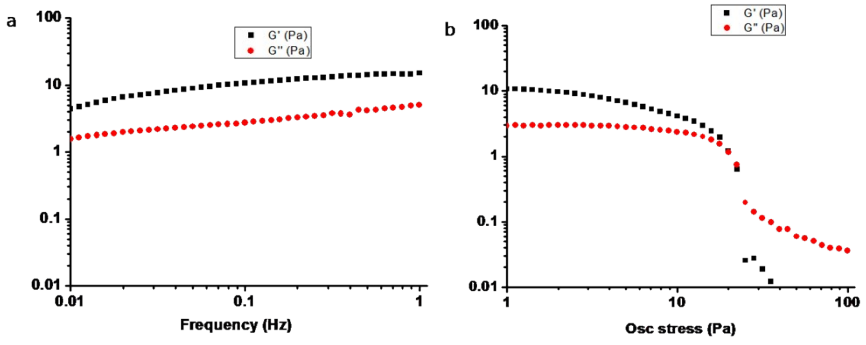


Figure S11: Rheology of LC-G-^{L}F (**1**, 2 wt%) (a) Frequency sweep (at 0.5 Pa) and (b) Stress sweep (at 0.1 Hz)

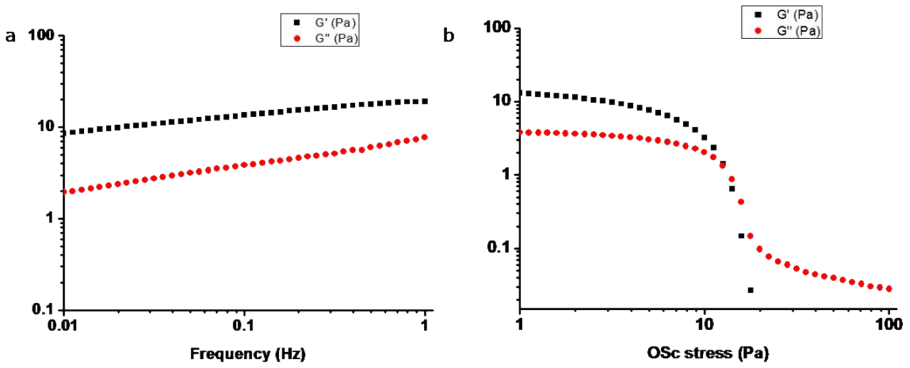


Figure S12: Rheology of LC-G-^{D}F (**2**, 2 wt%) (a) Frequency sweep (at 0.5 Pa) and (b) Stress sweep (at 0.1 Hz)

Table S4: Rheology data of LC-G-^{L}F (**1**) and LC-G-^{D}F (**2**)

Sample	G' (Pa)	G" (Pa)	G'/G"	σ* (Pa)
LC-G-^{L}F (1)	10	2.7	3.7	22
LC-G-^{D}F (2)	13.5	3.8	3.5	14

Rheology studies of LC-G-^{D}F gel in pH 8 with Ag(I) before and after photoreduction

Rheological studies were done for LC-G-^{D}F with Ag(I) doping before and after the illumination with 2 wt% of gelator at pH 8 (100 mM phosphate buffer) and 0.4 mM of Ag(I) doping. The viscoelastic behavior typical of a molecular gel was with storage modulus (G') values always greater than loss modulus (G") ones. The frequency sweep experiment and stress sweep experiments revealed that there was only a marginal increase in the dynamic storage modulus (G') and the loss modulus (G") after illumination (**Table S7**).

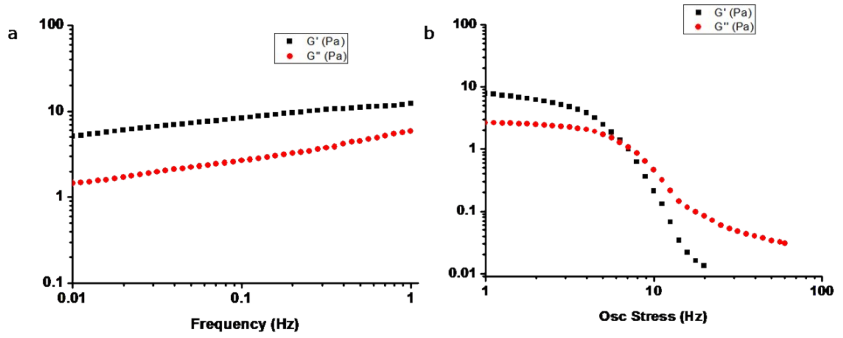


Figure S13: Rheology of LC-G-^{D}F (**2**, 2 wt%) with 0.4 mM Ag (I) before illumination (a) Frequency sweep (at 0.5 Pa) and (b) Stress sweep (at 0.1 Hz)

Table S5: Rheology data of LC-G-^{D}F with Ag(I)

Sample	G' (Pa)	G" (Pa)	G'/G"	σ* (Pa)
LC-G-^{D}F with Ag(I)	8.3	2.6	3.2	7

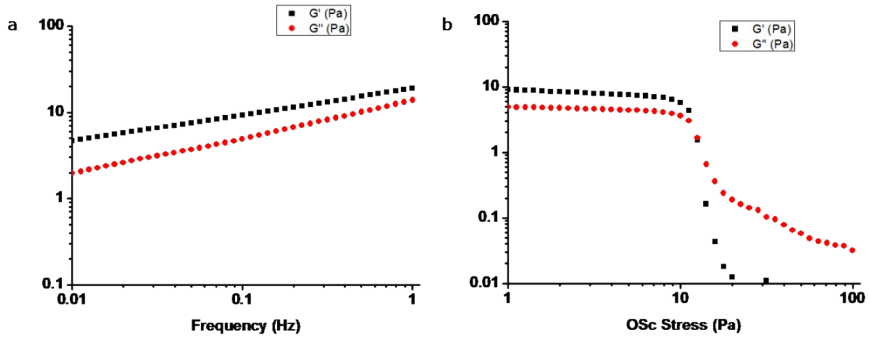


Figure S14: Rheology of LC-G-^{D}F (**2**, 2 wt%) with 0.4 mM Ag(I) after illumination for 6h (a) Frequency sweep (at 0.5 Pa) and (b) Stress sweep (at 0.1 Hz)

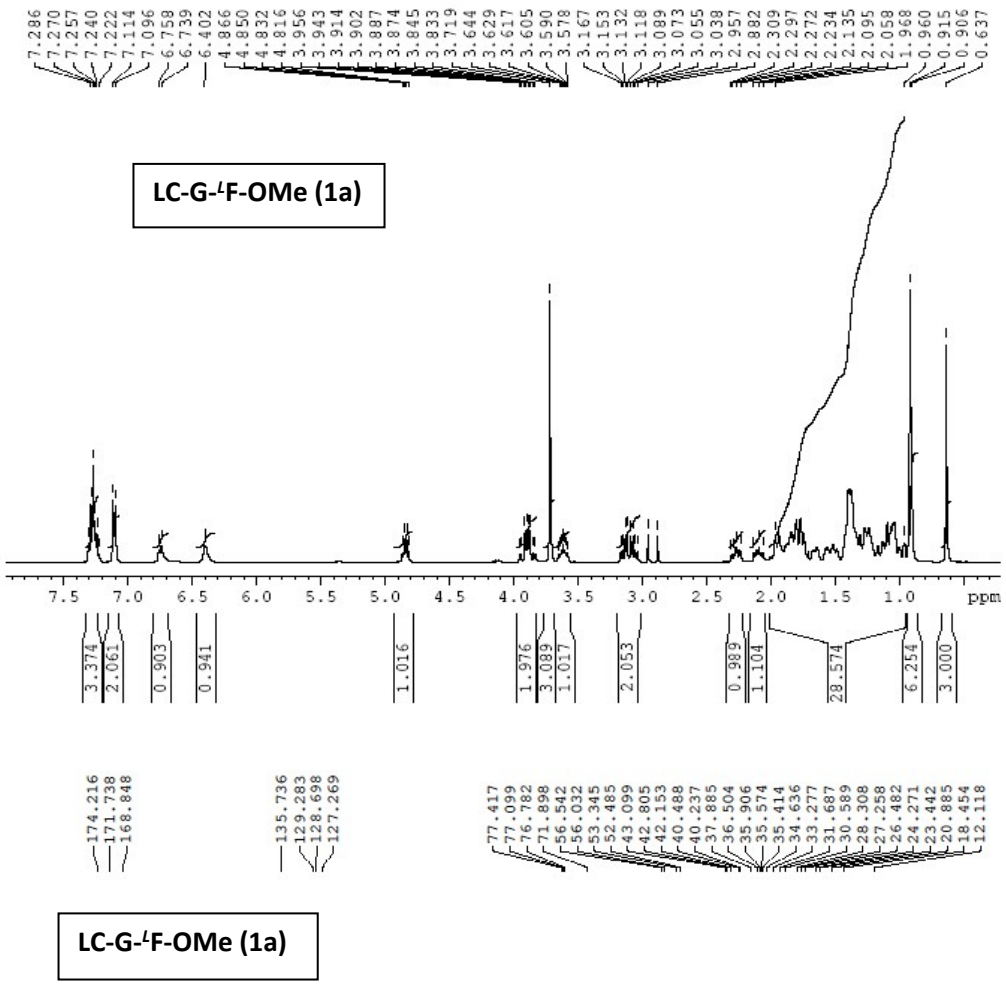
Table S6: Rheology data of LC-G-^{D}F with AgNPs after illumination

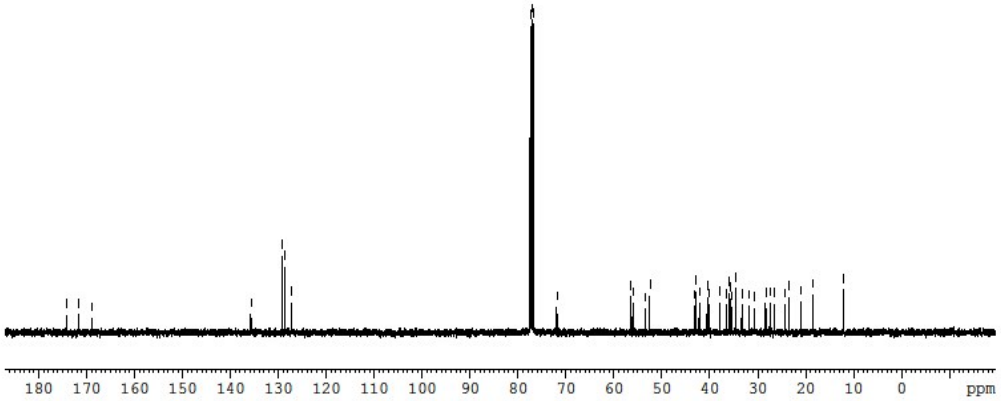
Sample	G' (Pa)	G" (Pa)	G'/G"	σ* (Pa)
LC-G-^{D}F with AgNPs	9.2	4.9	1.8	12.6

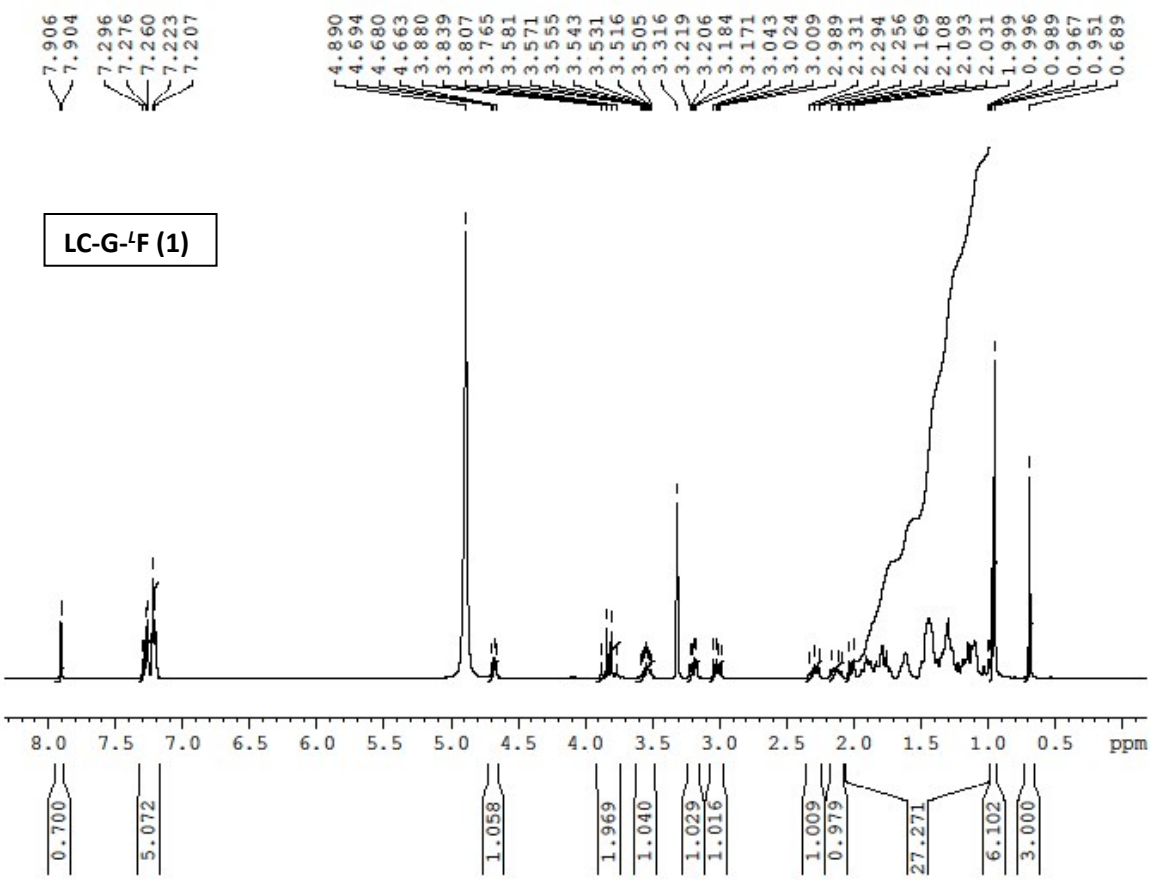
Table S7: Comparison table

Sample	G' (Pa)	G" (Pa)	G'/G"	σ* (Pa)
LC-G-^{D}F (**2**) [Table S4]	13.5	3.8	3.5	14
LC-G-^{D}F (**2**) with 0.4 mM Ag(I)	8.3	2.6	3.2	7
LC-G-^{D}F (**2**) with AgNPs after illumination	9.2	4.9	1.8	12.6

Copies of ^{1}H, ^{13}C NMR spectra



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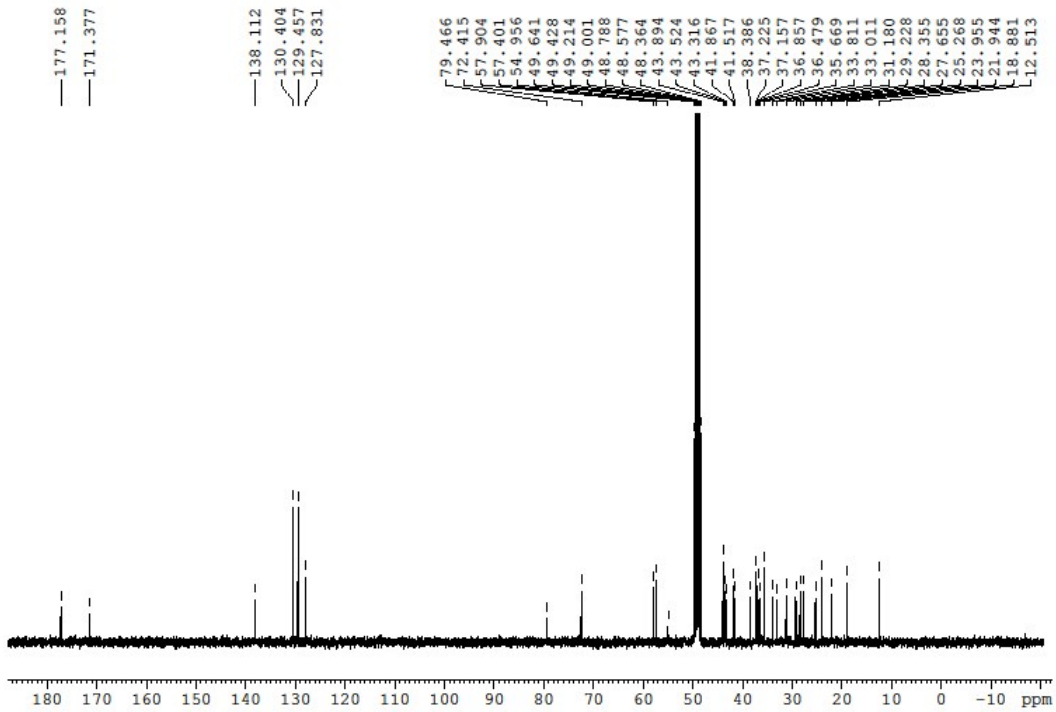
7.296
7.276
7.260
7.223
7.207
4.890
4.694
4.680
4.663
3.880
3.839
3.807
3.765
3.581
3.571
3.555
3.543
3.531
3.516
3.505
3.316
3.219
3.206
3.184
3.171
3.043
3.024
3.009
2.989
2.331
2.294
2.256
2.169
2.108
2.093
2.031
1.999
0.996
0.989
0.967
0.951
0.689
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.700
5.072
1.058
1.969
1.040
1.029
1.016
1.009
0.979
27.271
6.102
3.000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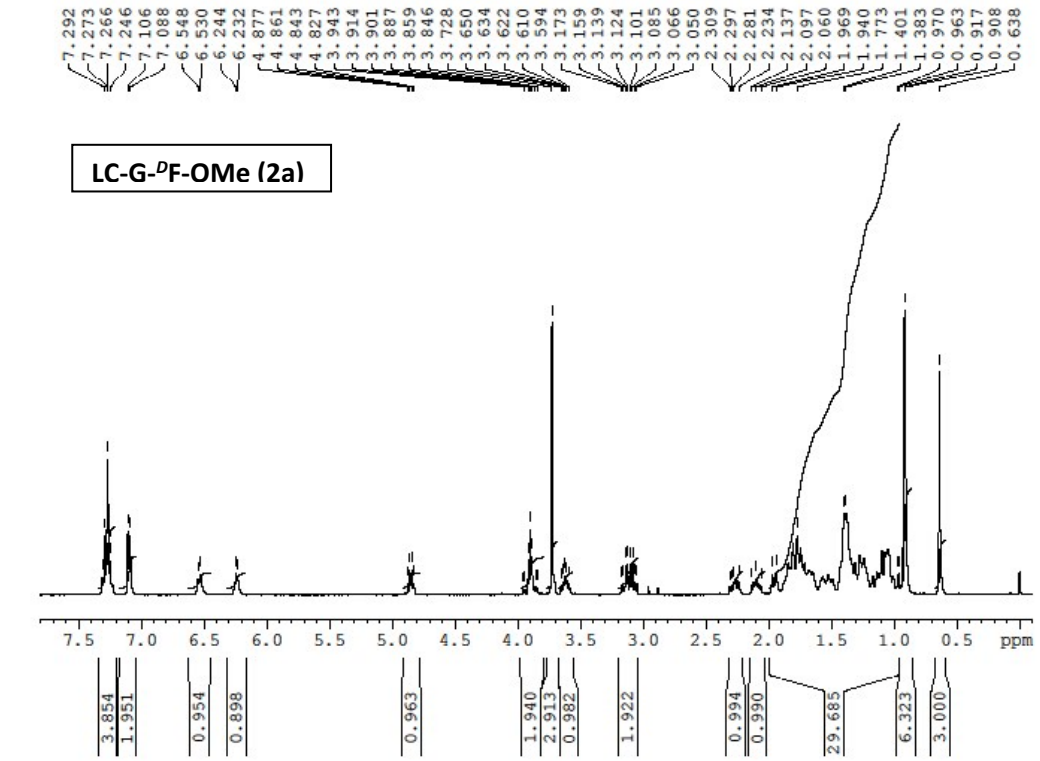
171.377
138.112
130.404
129.457
127.831
79.466
72.415
57.904
57.401
54.956
49.641
49.428
49.214
49.001
48.788
48.577
48.364
43.894
43.524
43.316
41.867
41.517
38.386
37.225
37.157
36.857
36.479
35.669
33.811
33.011
31.180
29.228
28.355
27.655
25.268
23.955
21.944
18.881
12.513
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm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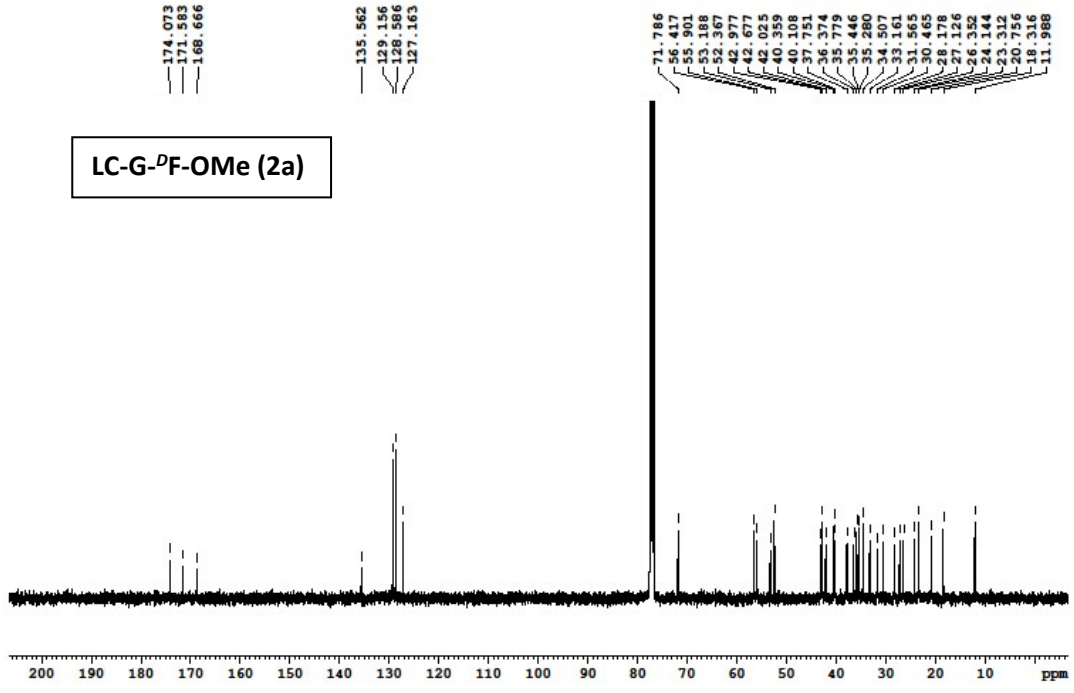
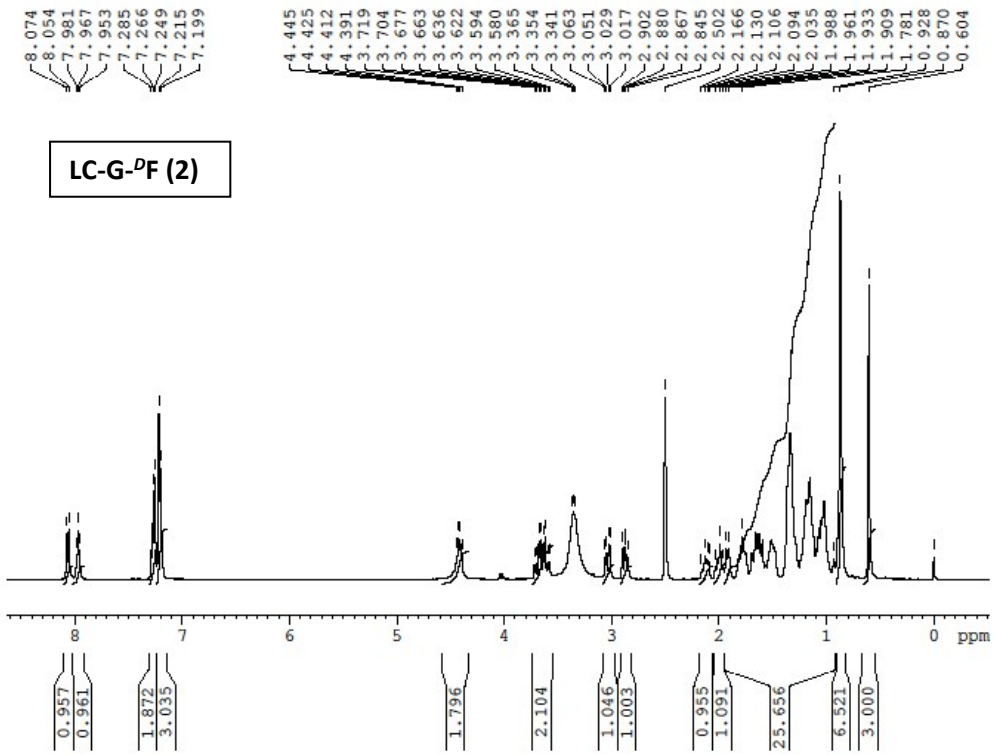
7.273
7.266
7.246
7.106
7.088
6.548
6.530
6.244
6.232
4.877
4.861
4.843
4.827
3.943
3.914
3.901
3.887
3.859
3.846
3.728
3.650
3.634
3.622
3.610
3.594
3.173
3.159
3.139
3.124
3.101
3.085
3.066
3.050
2.309
2.297
2.281
2.234
2.137
2.097
2.060
1.969
1.940
1.773
1.401
1.383
0.970
0.963
0.917
0.908
0.638
LC-G-DF-OMe (2a)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.854
1.951
0.954
0.898
0.963
1.940
2.913
0.982
1.922
0.994
0.990
29.685
6.323
3.000


174.073
171.583
168.666
135.562
129.156
128.586
127.163
71.786
56.417
55.901
53.188
52.367
42.977
42.677
42.025
40.359
40.108
37.751
36.374
35.779
35.446
35.280
34.507
33.161
31.565
30.465
28.178
27.126
26.352
24.144
23.312
20.756
18.316
11.988
LC-G-DF-OMe (2a)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.074
8.054
7.981
7.967
7.953
7.285
7.266
7.249
7.215
7.199
4.445
4.425
4.412
4.391
3.719
3.704
3.677
3.663
3.636
3.622
3.594
3.580
3.365
3.354
3.341
3.063
3.051
3.029
3.017
2.902
2.880
2.867
2.845
2.502
2.166
2.130
2.106
2.094
2.035
1.988
1.961
1.933
1.909
1.781
0.928
0.870
0.604
LC-G-DF (2)
8
7
6
5
4
3
2
1
0
ppm
0.957
0.961
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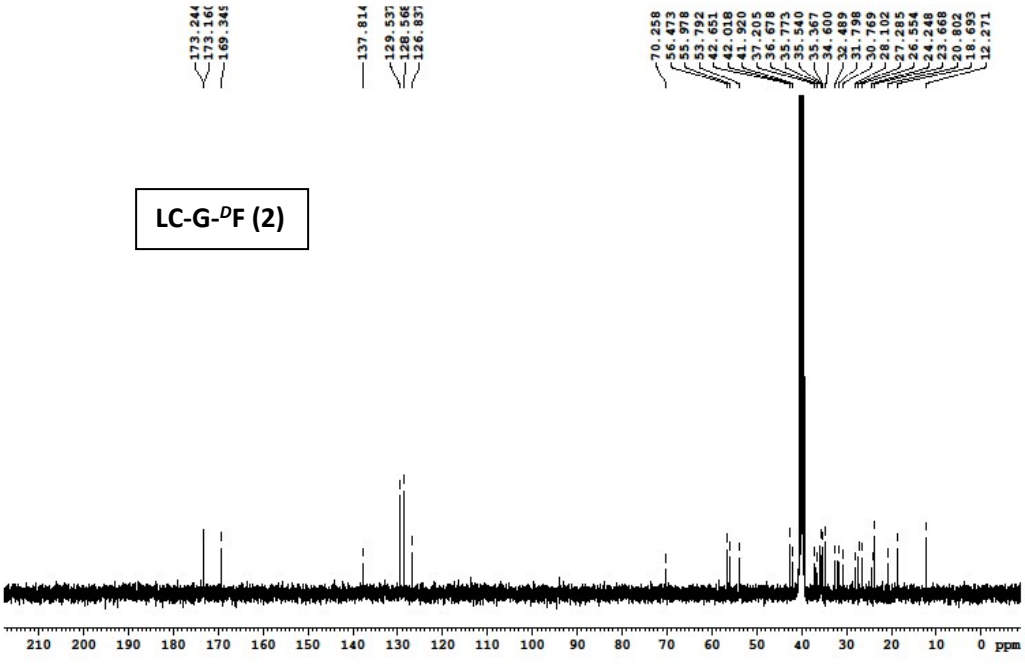
3.035
1.796
2.104
1.046
1.003
0.955
1.091
25.656
6.521
3.000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169.345
137.814
129.537
128.568
126.837
70.258
56.473
55.978
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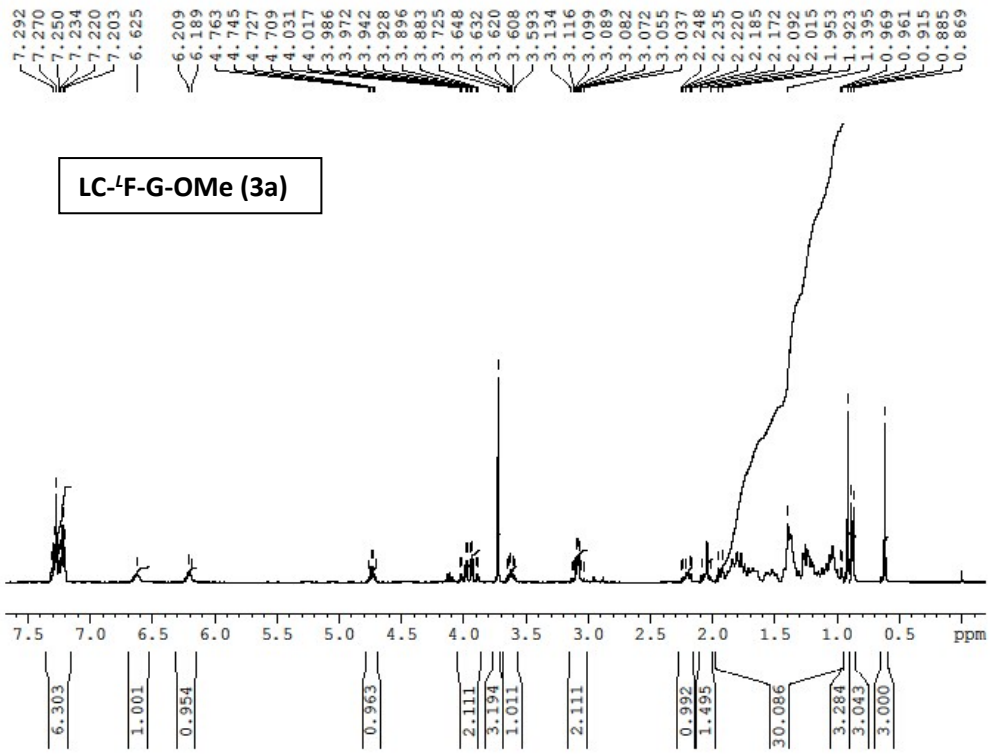
42.018
41.920
37.205
36.678
35.773
35.540
35.367
34.600
32.489
31.798
30.769
28.102
27.285
26.554
24.248
23.668
20.802
18.693
12.271
LC-G-DF (2)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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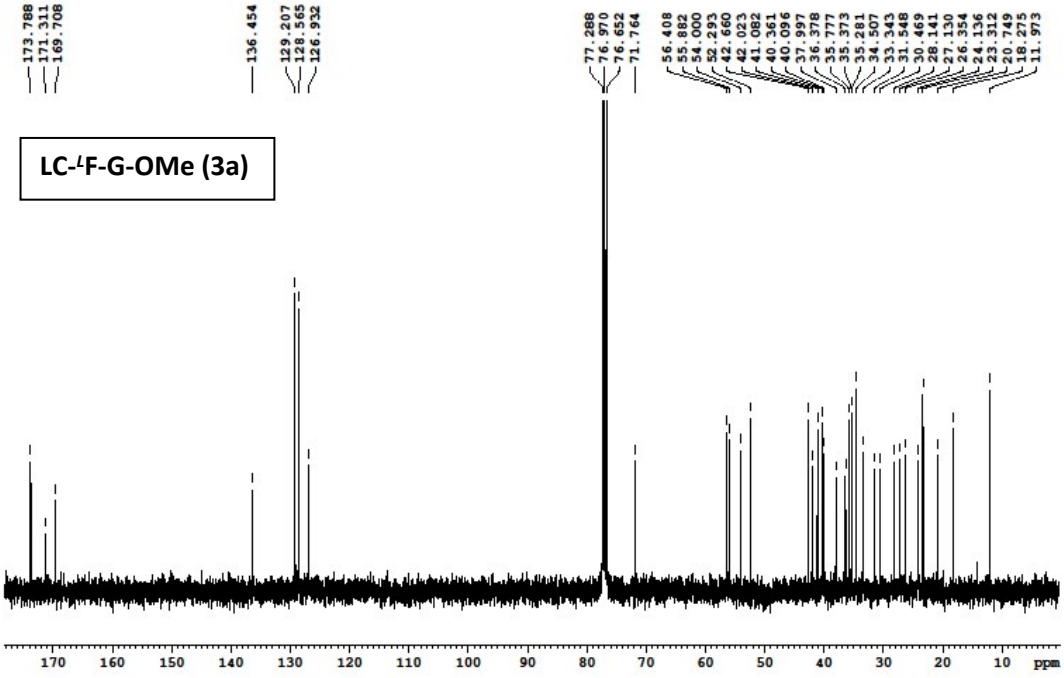
7.270
7.250
7.234
7.220
7.203
6.625
6.209
6.189
4.763
4.745
4.727
4.709
4.031
4.017
3.986
3.972
3.942
3.928
3.896
3.883
3.725
3.648
3.632
3.620
3.608
3.593
3.134
3.116
3.099
3.089
3.082
3.072
3.055
3.037
2.248
2.235
2.220
2.185
2.172
2.092
2.015
1.953
1.923
1.395
0.969
0.961
0.915
0.885
0.869
LC-ᴸF-G-OMe (3a)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.303
1.001
0.954
0.963
2.111
3.194
1.011
2.111
0.992
1.495
30.086
3.284
3.043
3.000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169.708
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129.207
128.565
126.932
77.288
76.970
76.652
71.764
56.408
55.882
54.000
52.293
42.660
42.023
41.082
40.361
40.096
37.997
36.378
35.777
35.373
35.281
34.507
33.343
31.548
30.469
28.141
27.130
26.354
24.136
23.312
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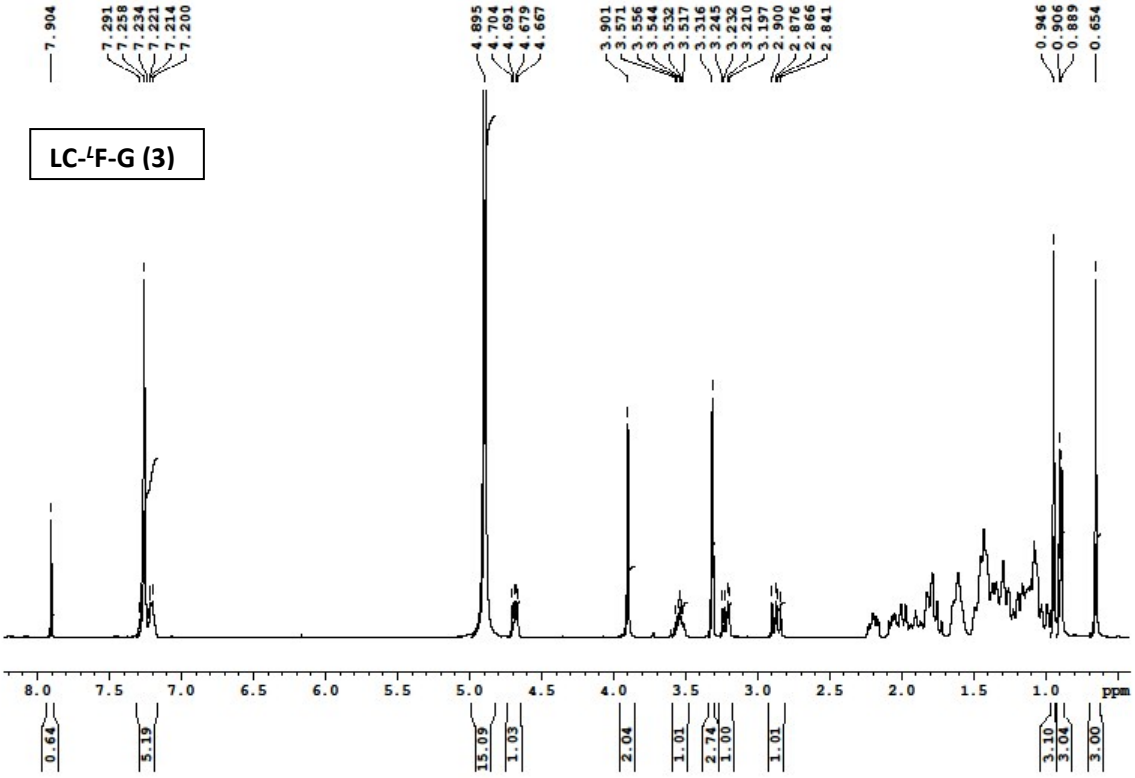
18.275
11.973
LC-ᴸF-G-OMe (3a)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


LC-ᴸF-G (3)
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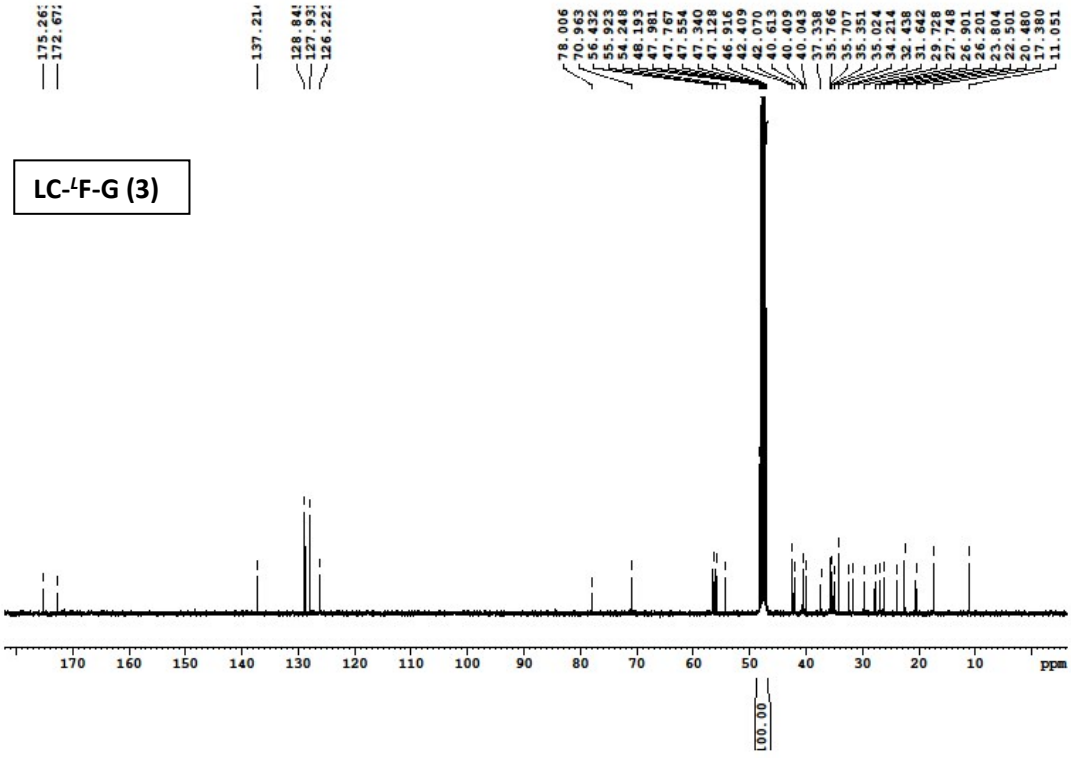
7.258
7.234
7.221
7.214
7.200
4.895
4.704
4.691
4.679
4.667
3.901
3.571
3.556
3.544
3.532
3.517
3.316
3.245
3.232
3.210
3.197
2.900
2.876
2.866
2.841
0.946
0.906
0.889
0.654
ppm
0.64
5.19
15.09
1.03
2.04
1.01
2.74
1.00
1.01
3.10
3.04
3.00


LC-ᴸF-G (3)
175.26
172.67
137.21
128.84
127.93
126.22
78.006
70.963
56.432
55.923
54.248
48.193
47.981
47.767
47.554
47.340
47.128
46.916
42.409
42.070
40.613
40.409
40.043
37.338
35.766
35.707
35.351
35.024
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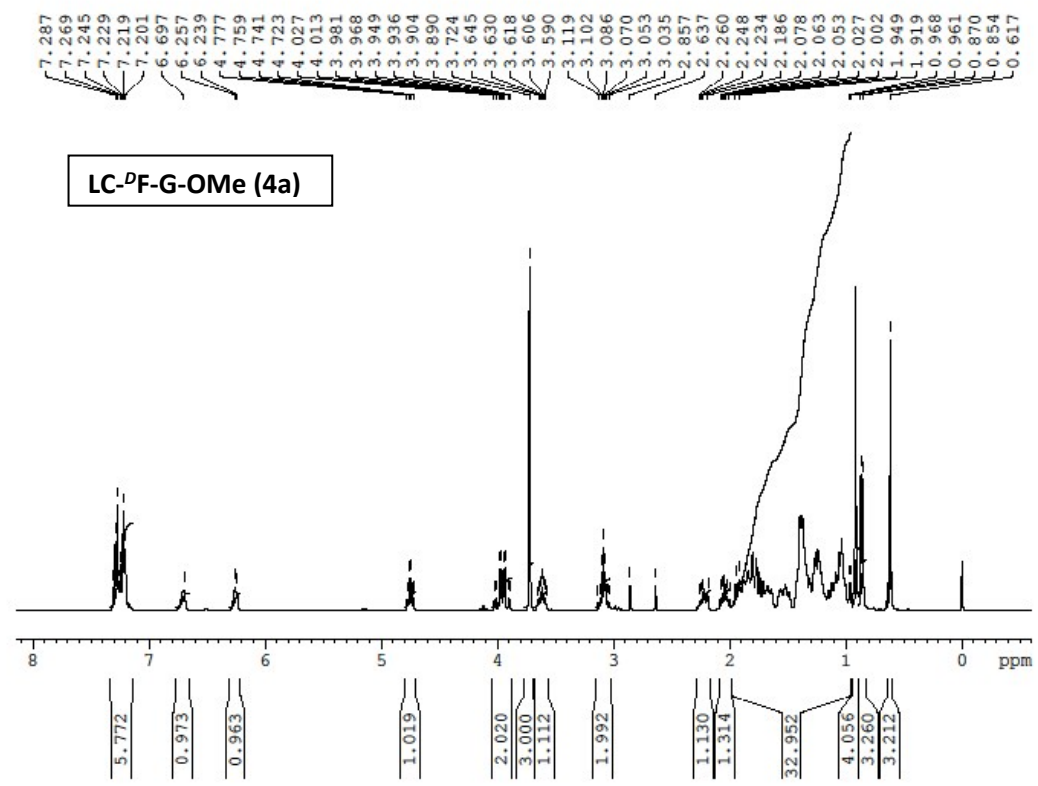
22.501
20.480
17.380
11.051
ppm
100.00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7.229
7.219
7.201
6.697
6.257
6.239
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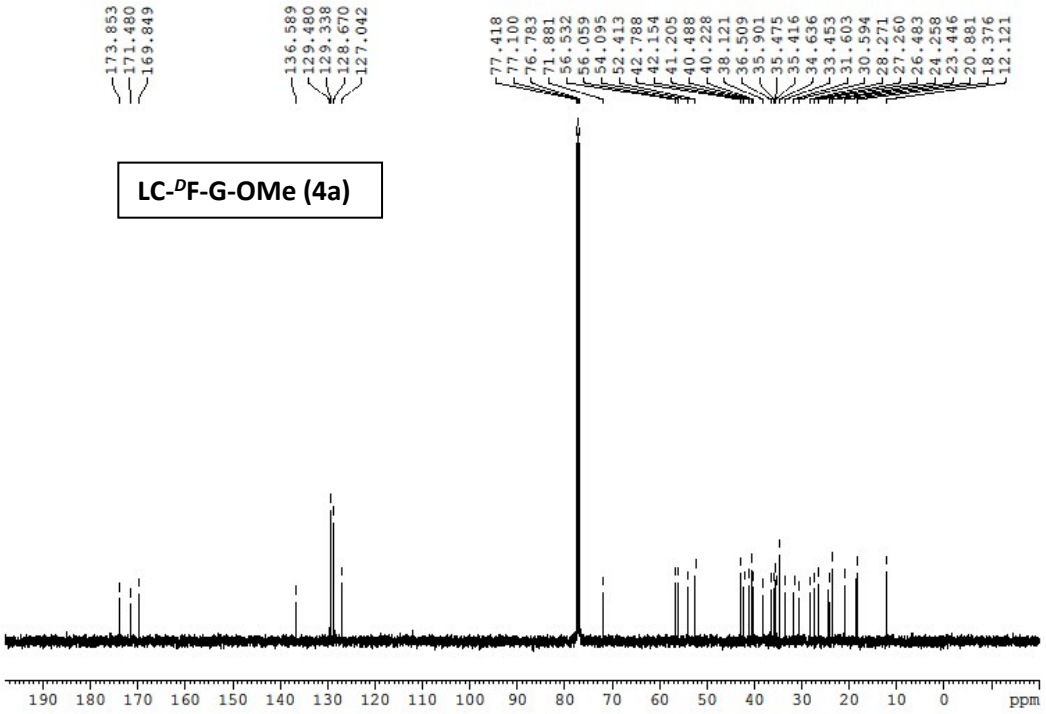
4.741
4.723
4.027
4.013
3.981
3.968
3.949
3.936
3.904
3.890
3.724
3.645
3.630
3.618
3.606
3.590
3.119
3.102
3.086
3.070
3.053
3.035
2.857
2.637
2.260
2.248
2.234
2.186
2.078
2.063
2.053
2.027
2.002
1.949
1.919
0.968
0.961
0.870
0.854
0.617
LC-DF-G-OMe (4a)
8
7
6
5
4
3
2
1
0
ppm
5.772
0.973
0.963
1.019
2.020
3.000
1.112
1.992
1.130
1.314
32.952
4.056
3.260
3.212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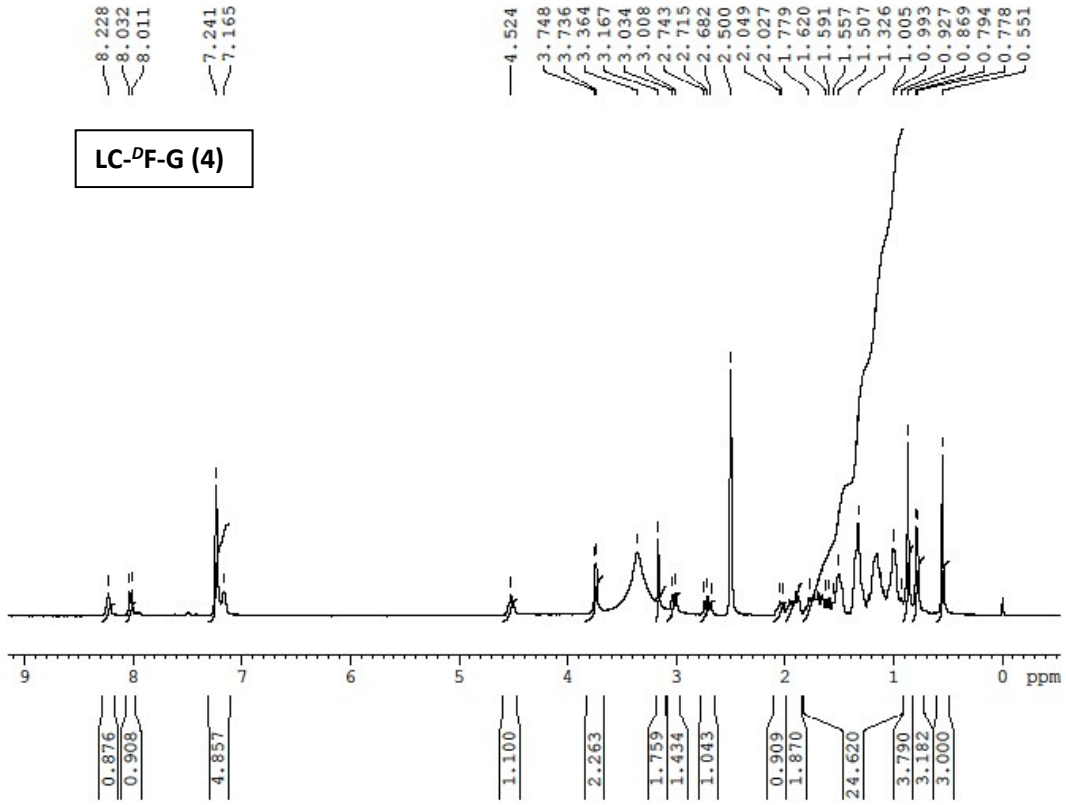
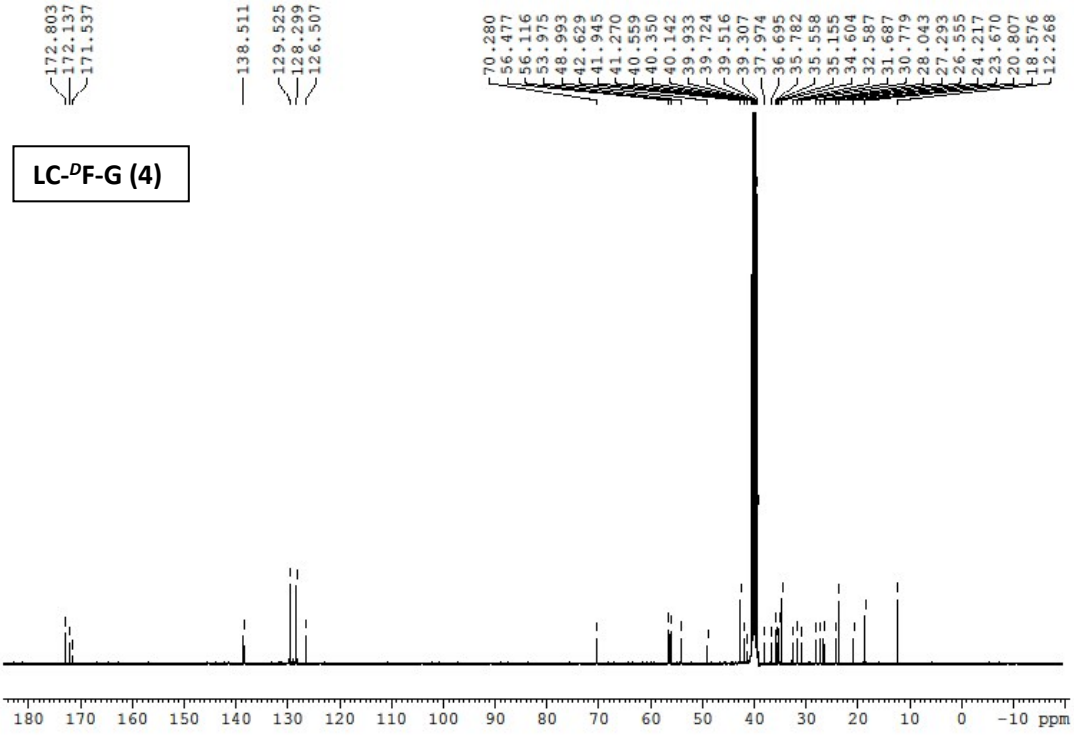
171.480
169.849
136.589
129.480
129.338
128.670
127.042
77.418
77.100
76.783
71.881
56.532
56.059
54.095
52.413
42.788
42.154
41.205
40.488
40.228
38.121
36.509
35.901
35.475
35.416
34.636
33.453
31.603
30.594
28.271
27.260
26.483
24.258
23.446
20.881
18.376
12.121
LC-DF-G-OMe (4a)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.228
8.032
8.011
7.241
7.165
4.524
3.748
3.736
3.364
3.167
3.034
3.008
2.743
2.715
2.682
2.500
2.049
2.027
1.779
1.620
1.591
1.557
1.507
1.326
1.005
0.993
0.927
0.869
0.794
0.778
0.551
LC-DF-G (4)
9
8
7
6
5
4
3
2
1
0
ppm
0.876
0.908
4.857
1.100
2.263
1.759
1.434
1.043
0.909
1.870
24.620
3.790
3.182
3.000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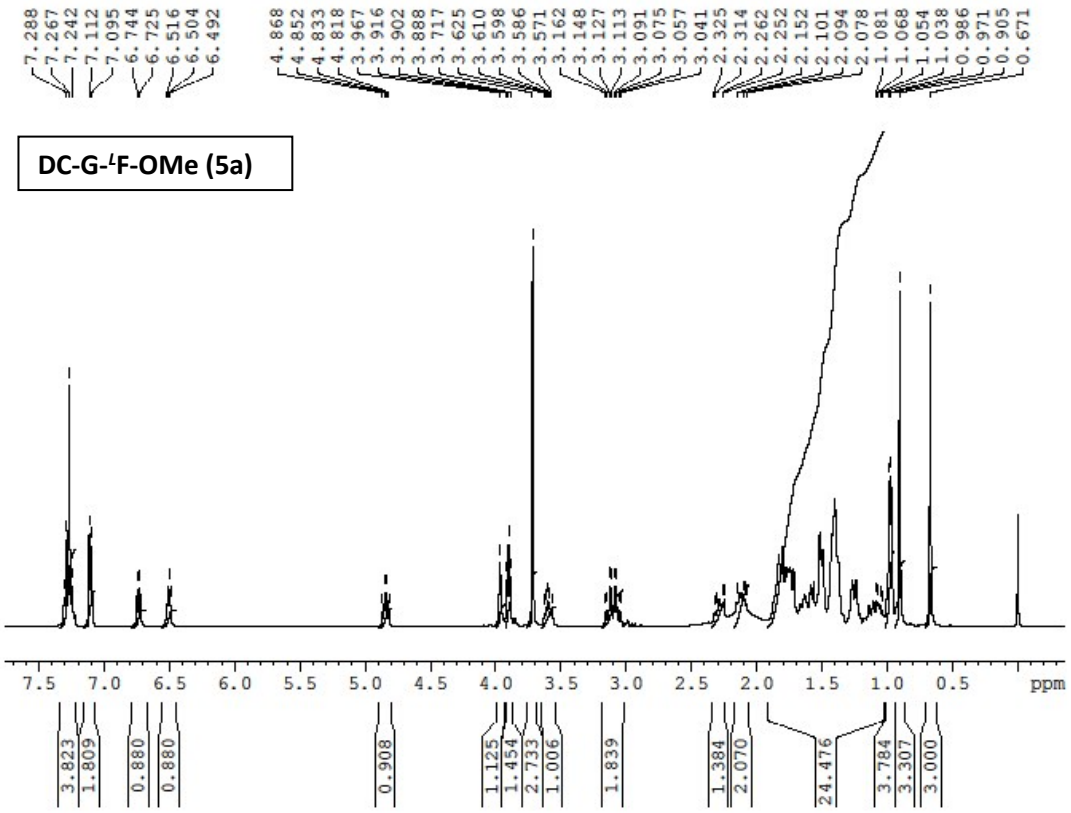
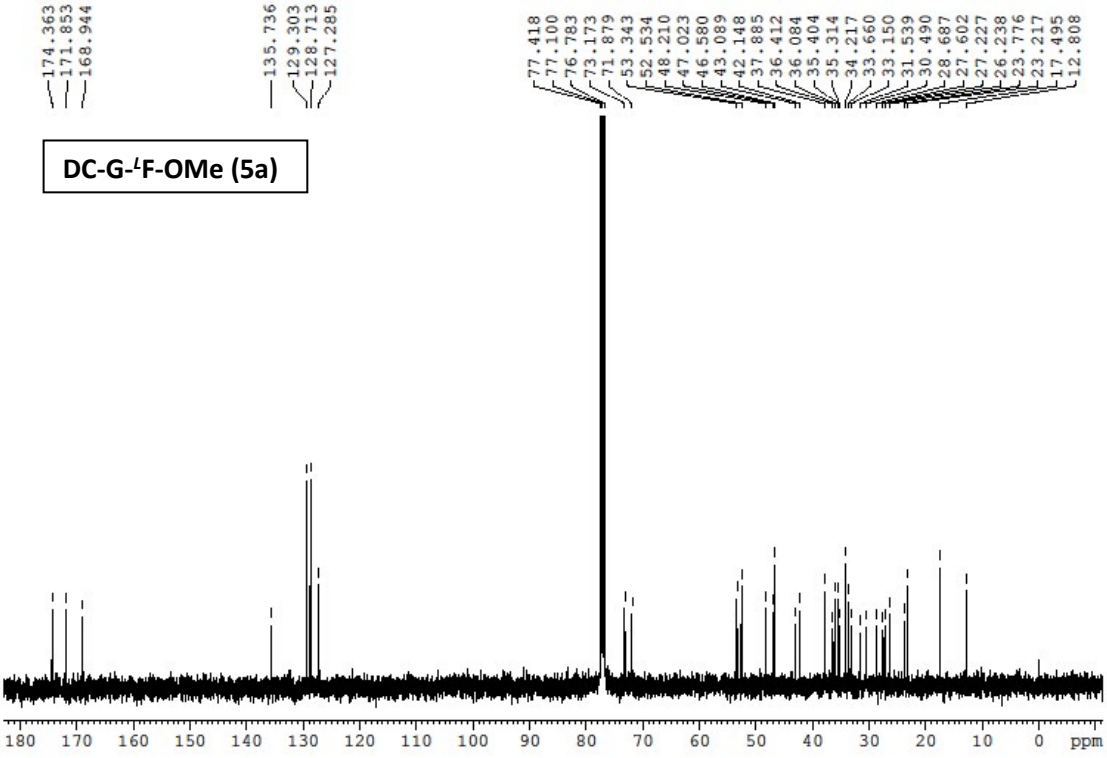
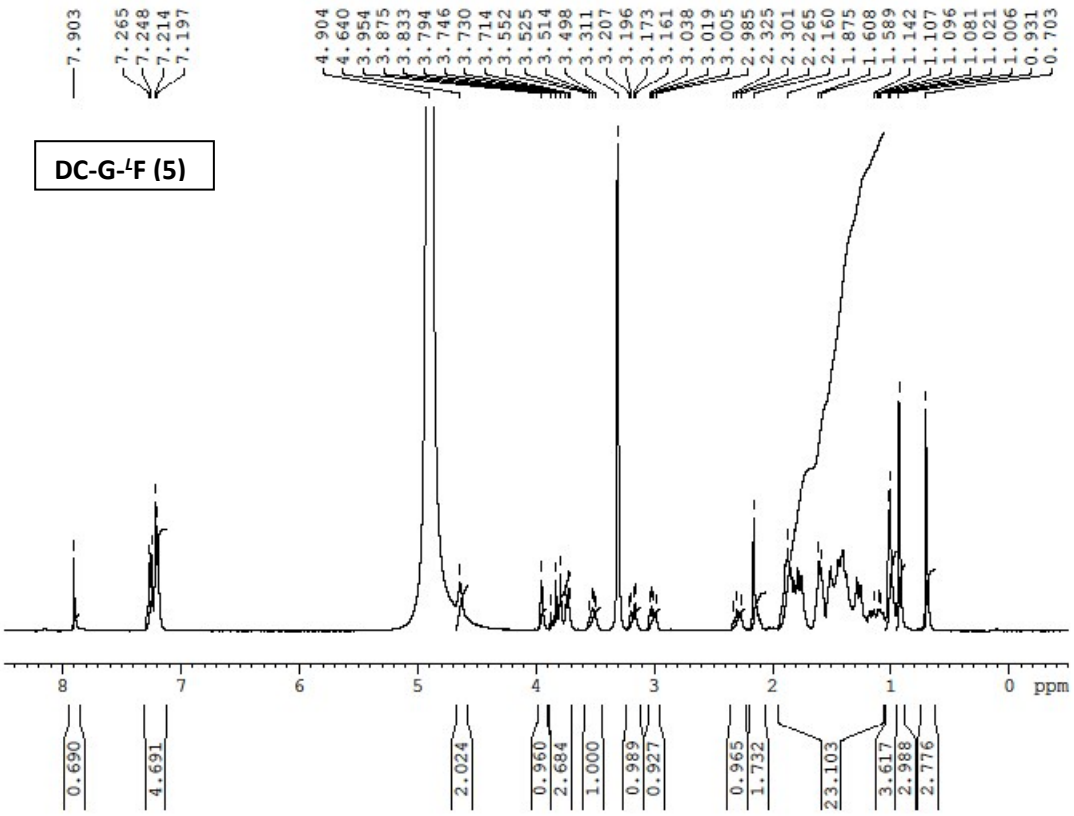
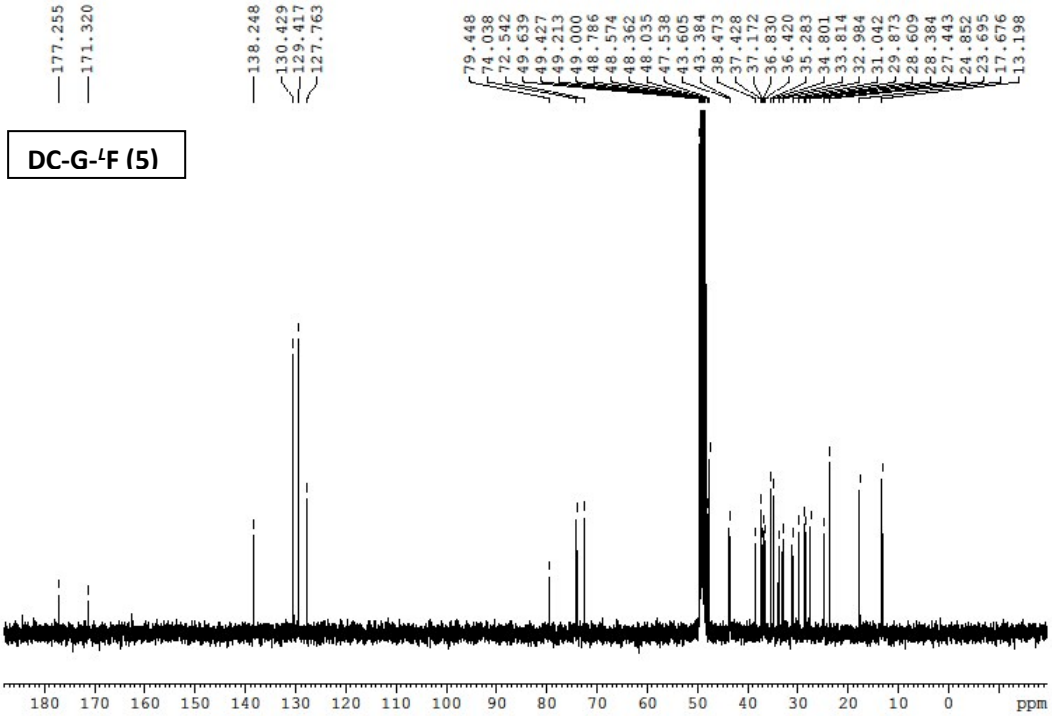
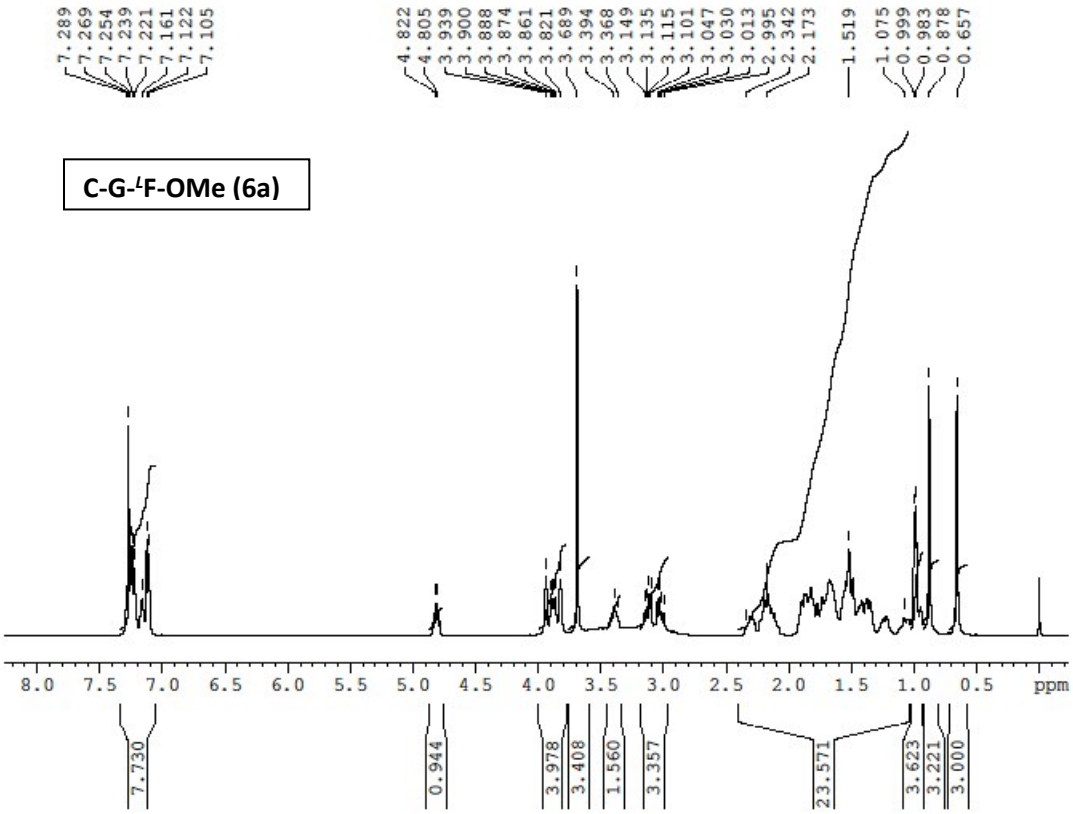
172.137
171.537
138.511
129.525
128.299
126.507
70.280
56.477
56.116
53.975
48.993
42.629
41.945
41.270
40.559
40.350
40.142
39.933
39.724
39.516
39.307
37.974
36.695
35.782
35.558
35.155
34.604
32.587
31.687
30.779
28.043
27.293
26.555
24.217
23.670
20.807
18.576
12.268
LC-DF-G (4)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

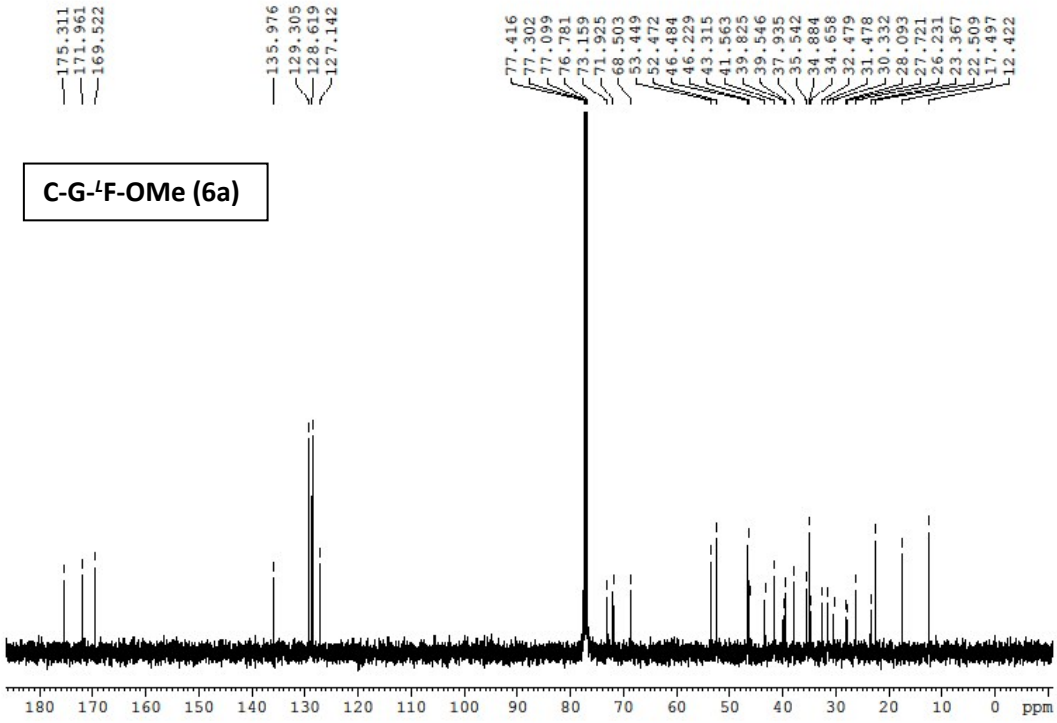

7.288
7.267
7.242
7.112
7.095
6.744
6.725
6.516
6.504
6.492
4.868
4.852
4.833
4.818
3.967
3.916
3.902
3.888
3.717
3.625
3.610
3.598
3.586
3.571
3.162
3.148
3.127
3.113
3.091
3.075
3.057
3.041
2.325
2.314
2.262
2.252
2.152
2.101
2.094
2.078
1.081
1.068
1.054
1.038
0.986
0.971
0.905
0.671
DC-G-LF-OMe (5a)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.823
1.809
0.880
0.880
0.908
1.125
1.454
2.733
1.006
1.839
1.384
2.070
24.476
3.784
3.307
3.000

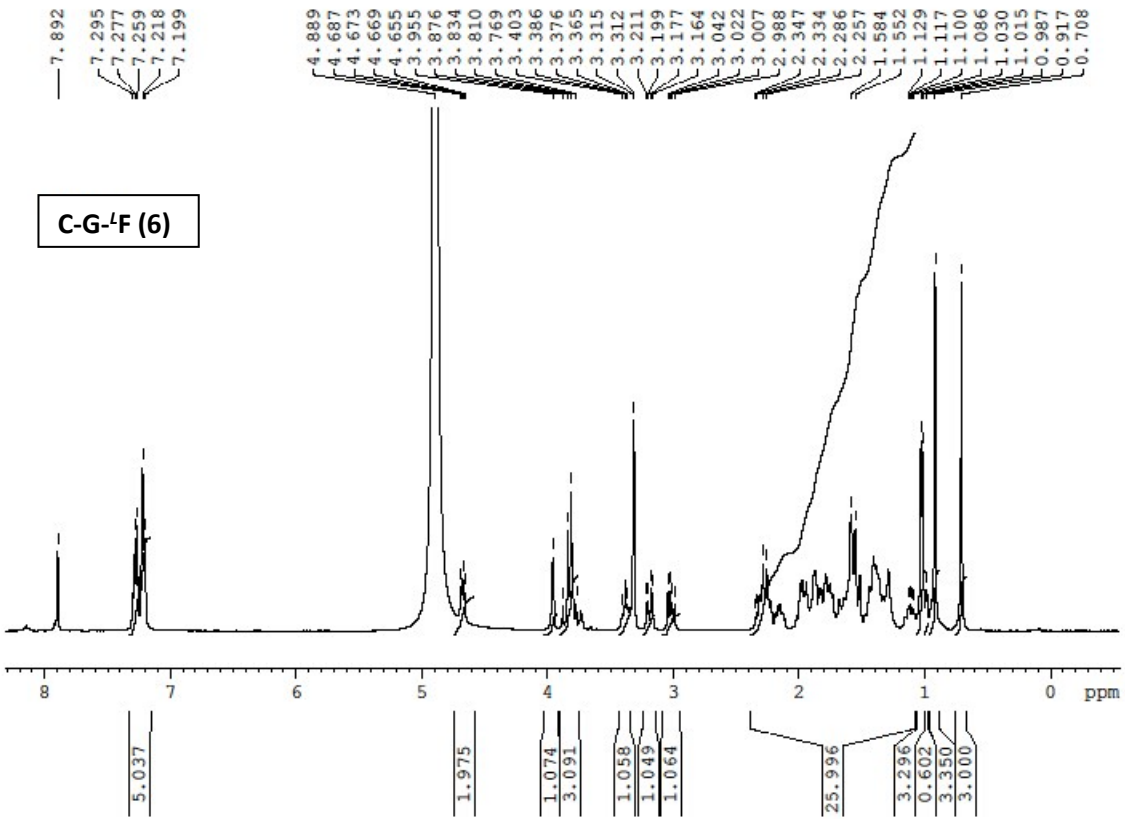

174.363
171.853
168.944
135.736
129.303
128.713
127.285
77.418
77.100
76.783
73.173
71.879
53.343
52.534
48.210
47.023
46.580
43.089
42.148
37.885
36.412
36.084
35.404
35.314
34.217
33.660
33.150
31.539
30.490
28.687
27.602
27.227
26.238
23.776
23.217
17.495
12.808
DC-G-LF-OMe (5a)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

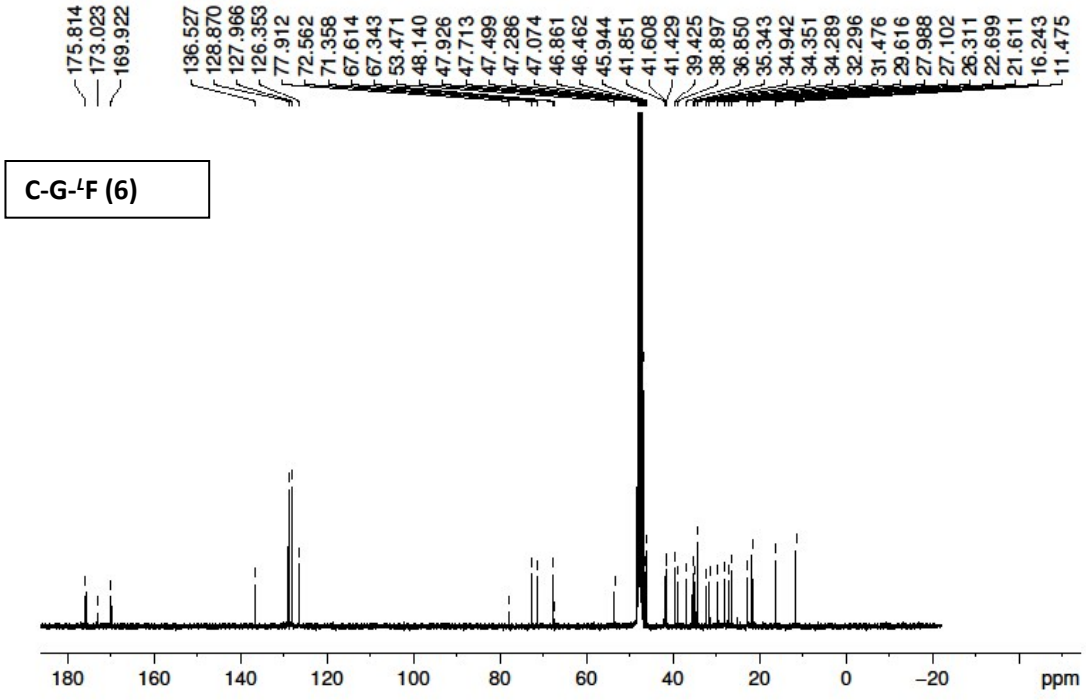

DC-G-^{L}F (5)
7.903
7.265
7.248
7.214
7.197
4.904
4.640
3.954
3.875
3.833
3.794
3.746
3.730
3.714
3.552
3.525
3.514
3.498
3.311
3.207
3.196
3.173
3.161
3.038
3.019
3.005
2.985
2.325
2.301
2.265
2.160
1.875
1.608
1.589
1.142
1.107
1.096
1.081
1.021
1.006
0.931
0.703
8
7
6
5
4
3
2
1
0
ppm
0.690
4.691
2.024
0.960
2.684
1.000
0.989
0.927
0.965
1.732
23.103
3.617
2.988
2.776


DC-G-^{L}F (5)
177.255
171.320
138.248
130.429
129.417
127.763
79.448
74.038
72.542
49.639
49.427
49.213
49.000
48.786
48.574
48.362
48.035
47.538
43.605
43.384
38.473
37.428
37.172
36.830
36.420
35.283
34.801
33.814
32.984
31.042
29.873
28.609
28.384
27.443
24.852
23.695
17.676
13.198
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.289
7.269
7.254
7.239
7.221
7.161
7.122
7.105
4.822
4.805
3.939
3.900
3.888
3.874
3.861
3.821
3.689
3.394
3.368
3.149
3.135
3.115
3.101
3.047
3.030
3.013
2.995
2.342
2.173
1.519
1.075
0.999
0.983
0.878
0.657
C-G-ᴸF-OMe (6a)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
7.730
0.944
3.978
3.408
1.560
3.357
23.571
3.623
3.221
3.000


175.311
171.961
169.522
135.976
129.305
128.619
127.142
77.416
77.302
77.099
76.781
73.159
71.925
68.503
53.449
52.472
46.484
46.229
43.315
41.563
39.825
39.546
37.935
35.542
34.884
34.658
32.479
31.478
30.332
28.093
27.721
26.231
23.367
22.509
17.497
12.422
C-G-ᴸF-OMe (6a)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.892
7.295
7.277
7.259
7.218
7.199
4.889
4.687
4.673
4.669
4.655
3.955
3.876
3.834
3.810
3.769
3.403
3.386
3.376
3.365
3.315
3.312
3.211
3.199
3.177
3.164
3.042
3.022
3.007
2.988
2.347
2.334
2.286
2.257
1.584
1.552
1.129
1.117
1.100
1.086
1.030
1.015
0.987
0.917
0.708
C-G-LF (6)
8
7
6
5
4
3
2
1
0
ppm
5.037
1.975
1.074
3.091
1.058
1.049
1.064
25.996
3.296
0.602
3.350
3.000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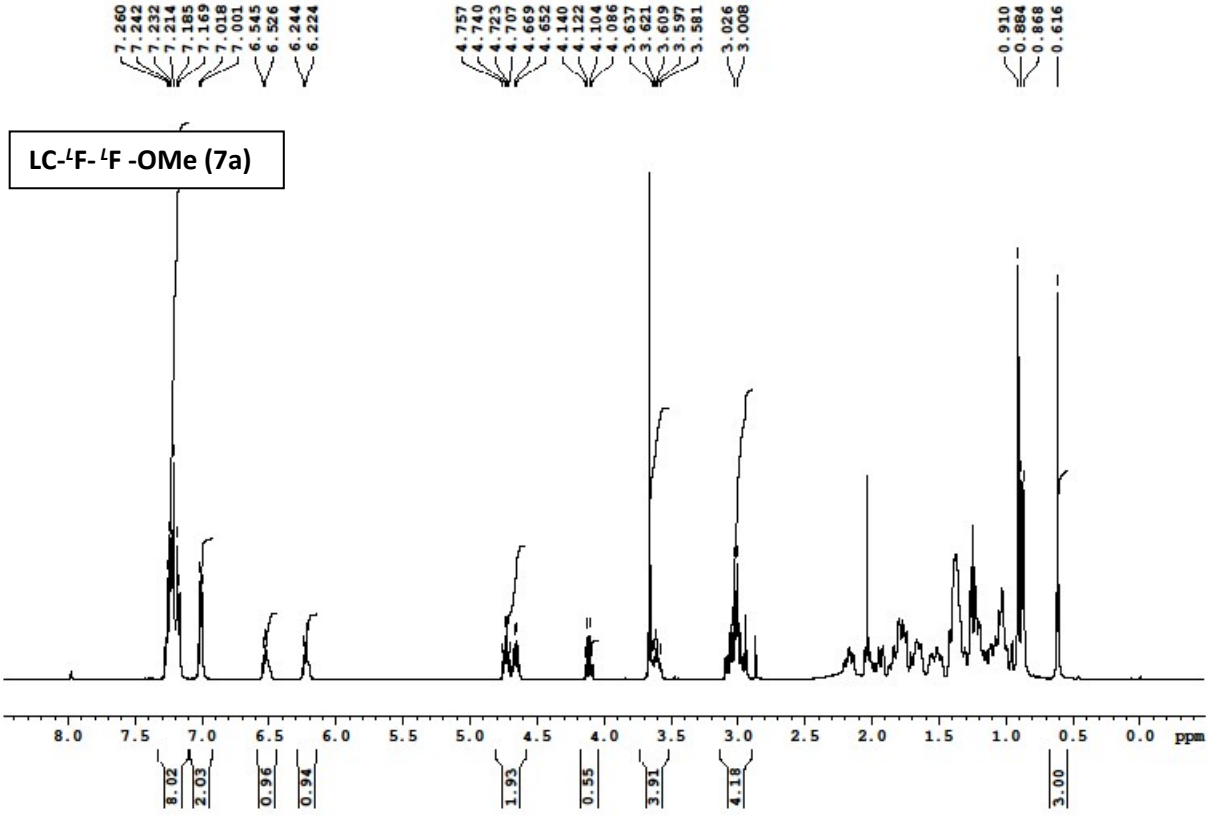
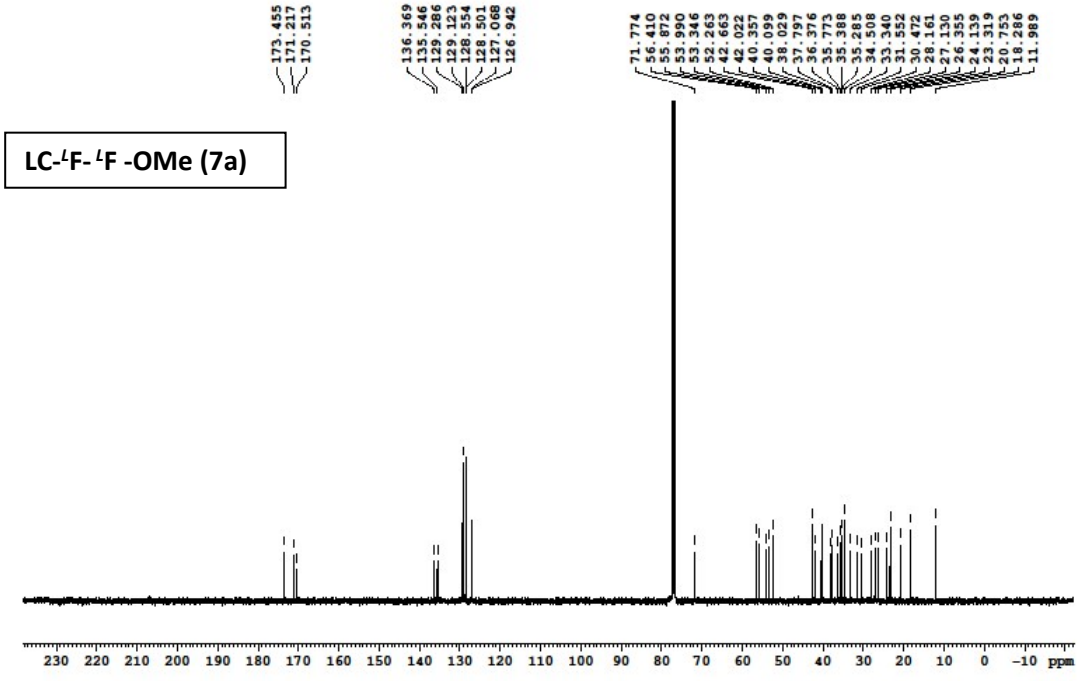
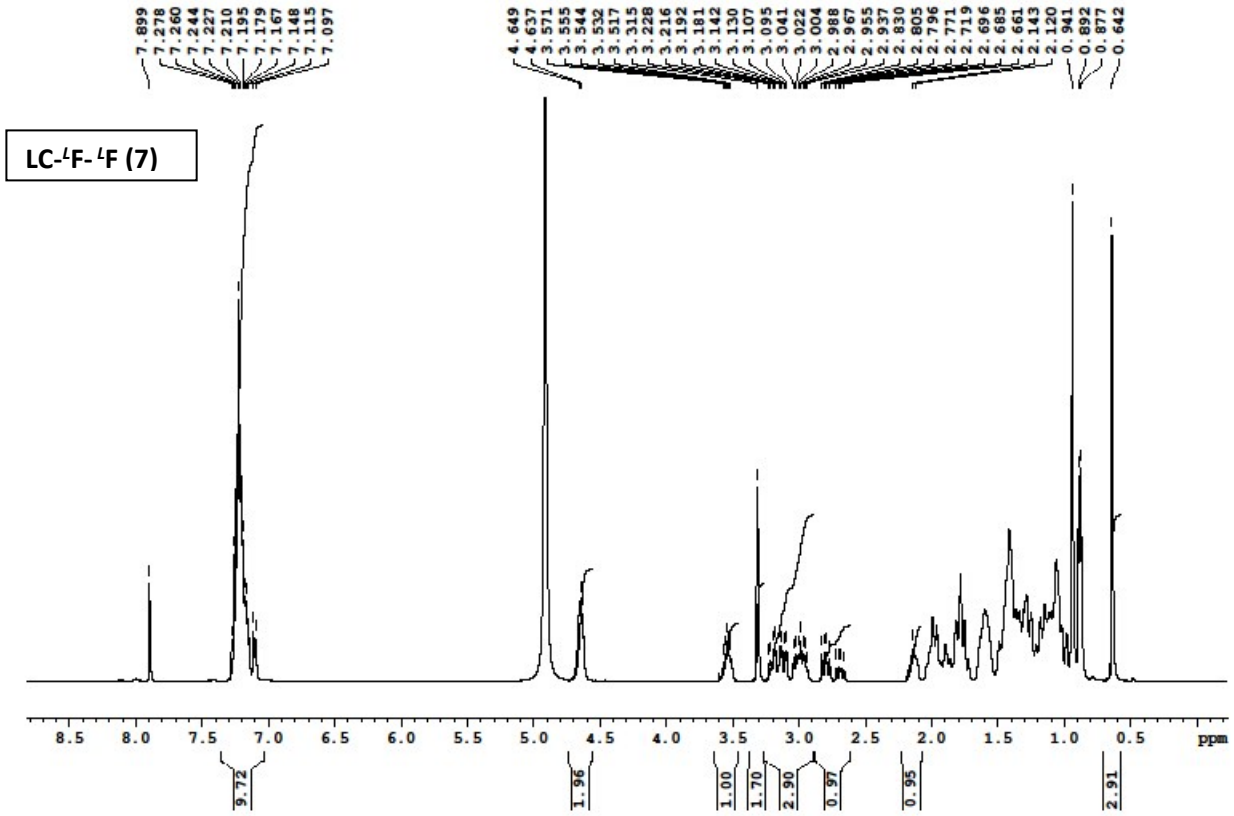
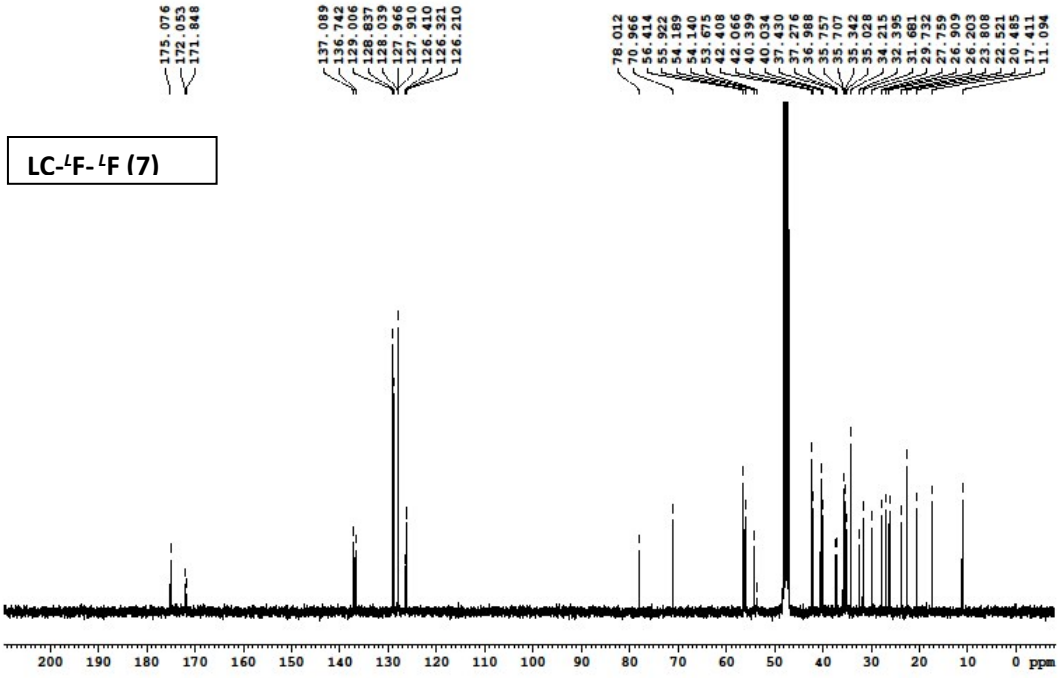
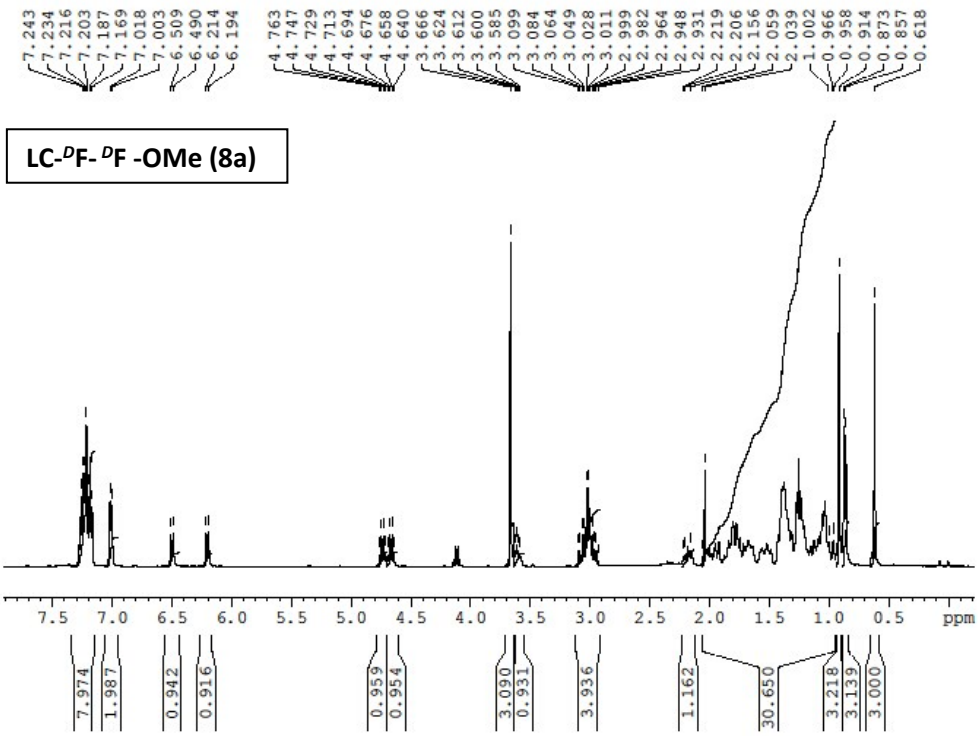
173.023
169.922
136.527
128.870
127.966
126.353
77.912
72.562
71.358
67.614
67.343
53.471
48.140
47.926
47.713
47.499
47.286
47.074
46.861
46.462
45.944
41.851
41.608
41.429
39.425
38.897
36.850
35.343
34.942
34.351
34.289
32.296
31.476
29.616
27.988
27.102
26.311
22.699
21.611
16.243
11.475
C-G-LF (6)
180
160
140
120
100
80
60
40
20
0
−20
ppm

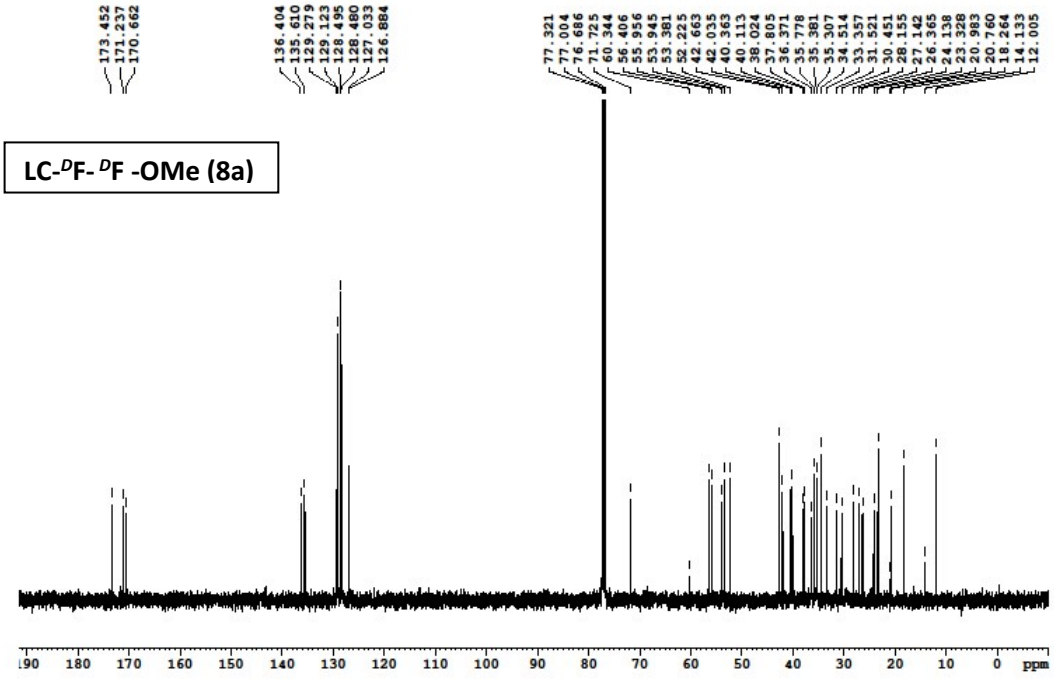

LC-ᴸF-ᴸF -OMe (7a)
7.260
7.242
7.232
7.214
7.185
7.169
7.018
7.001
6.545
6.526
6.244
6.224
4.757
4.740
4.723
4.707
4.669
4.652
4.140
4.122
4.104
4.086
3.637
3.621
3.609
3.597
3.581
3.026
3.008
0.910
0.884
0.868
0.616
8.02
2.03
0.96
0.94
1.93
0.55
3.91
4.18
3.00
ppm

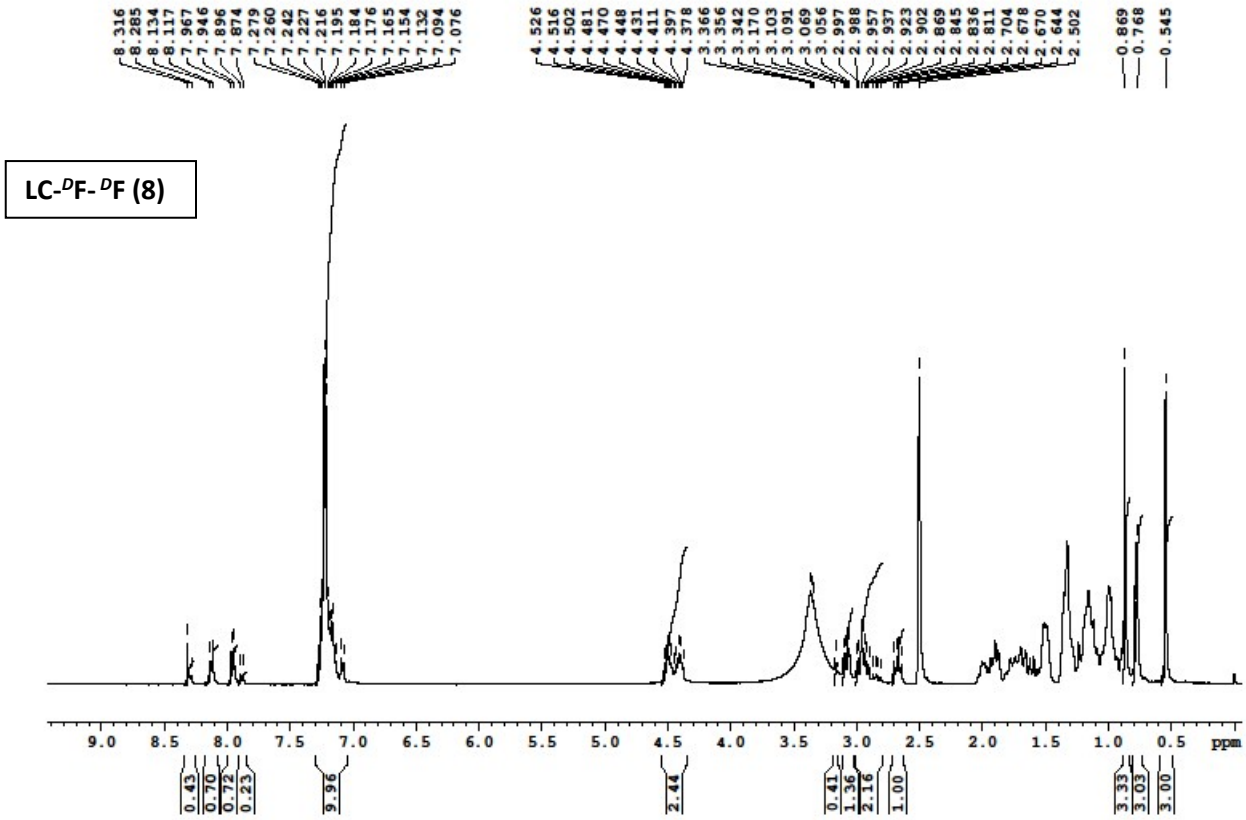

LC-ᴸF-ᴸF -OMe (7a)
173.455
171.217
170.513
136.369
135.546
129.286
129.123
128.554
128.501
127.068
126.942
71.774
56.410
55.872
55.990
53.346
52.263
42.663
42.022
40.357
40.099
38.029
37.797
36.376
35.773
35.388
35.285
34.508
33.340
31.552
30.472
28.161
27.130
26.355
24.139
23.319
20.753
18.286
11.989
ppm

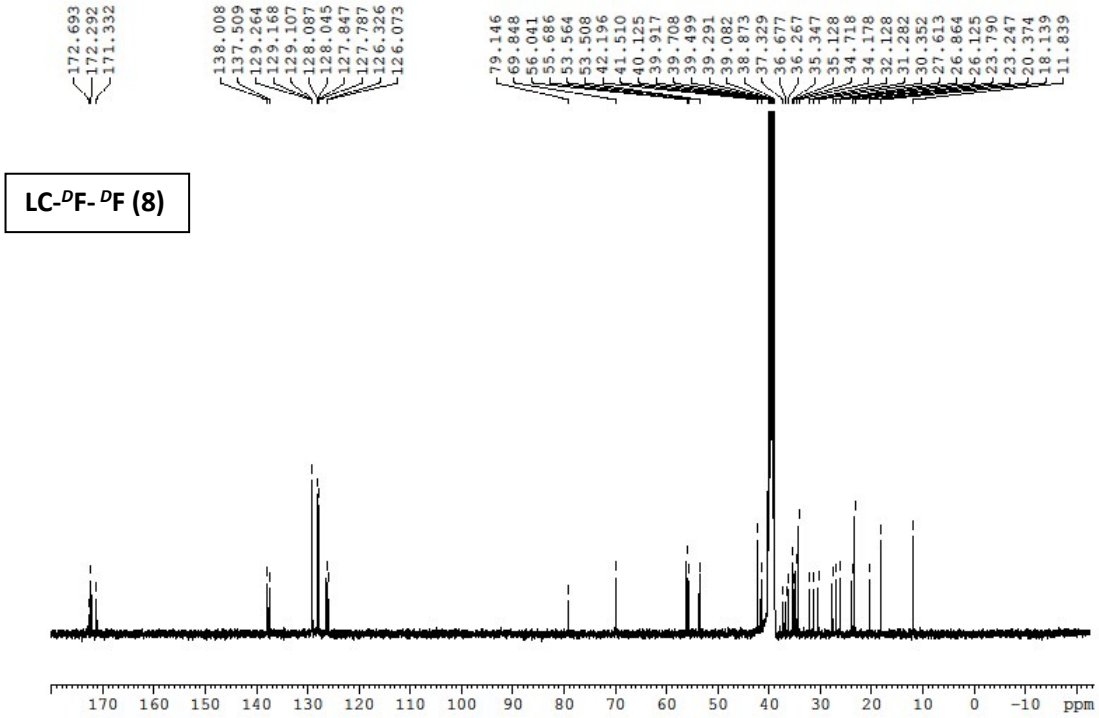

LC-ᴸF-ᴸF (7)
7.899
7.278
7.260
7.244
7.227
7.210
7.195
7.179
7.167
7.148
7.115
7.097
4.649
4.637
3.571
3.555
3.544
3.532
3.517
3.315
3.228
3.216
3.192
3.181
3.142
3.130
3.107
3.095
3.041
3.022
3.004
2.988
2.967
2.955
2.937
2.830
2.805
2.796
2.771
2.719
2.696
2.685
2.661
2.143
2.120
0.941
0.892
0.877
0.642
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
9.72
1.96
1.00
1.70
2.90
0.97
0.95
2.91

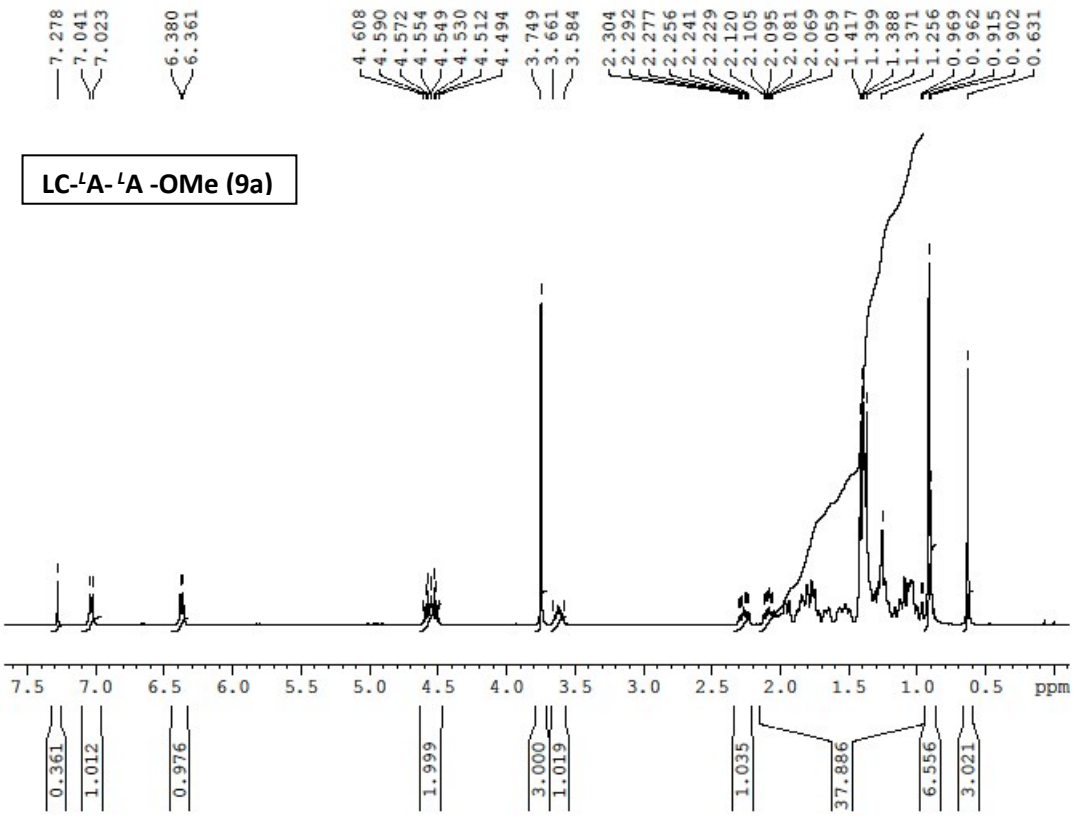

LC-ᴸF-ᴸF (7)
175.076
172.053
171.848
137.089
136.742
129.006
128.837
128.039
127.966
127.910
126.410
126.321
126.210
78.012
70.966
56.414
55.922
54.189
54.140
53.675
42.408
42.066
40.399
40.034
37.430
37.276
36.988
35.757
35.707
35.342
35.028
34.215
32.395
31.681
29.732
27.759
26.909
26.203
23.808
22.521
20.485
17.411
11.094
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

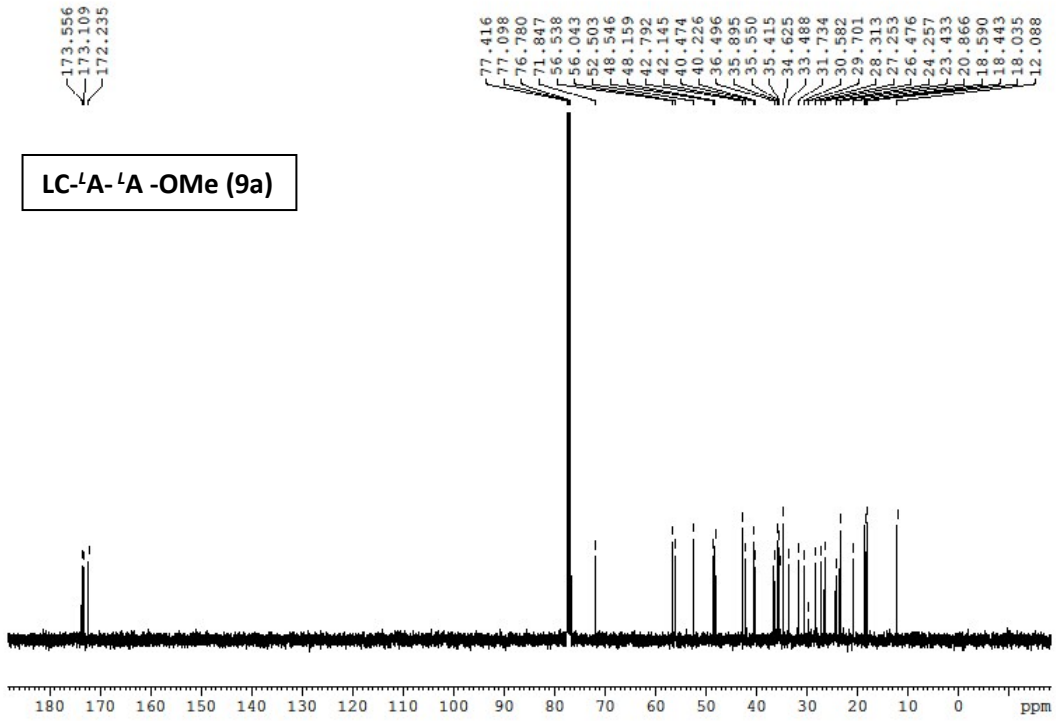

LC-DF-DF -OMe (8a)
7.243
7.234
7.216
7.203
7.187
7.169
7.018
7.003
6.509
6.490
6.214
6.194
4.763
4.747
4.729
4.713
4.694
4.676
4.658
4.640
3.666
3.624
3.612
3.600
3.585
3.099
3.084
3.064
3.049
3.028
3.011
2.999
2.982
2.964
2.948
2.931
2.219
2.206
2.156
2.059
2.039
1.002
0.966
0.958
0.914
0.873
0.857
0.618
ppm
7.974
1.987
0.942
0.916
0.959
0.954
3.090
0.931
3.936
1.162
30.650
3.218
3.139
3.000

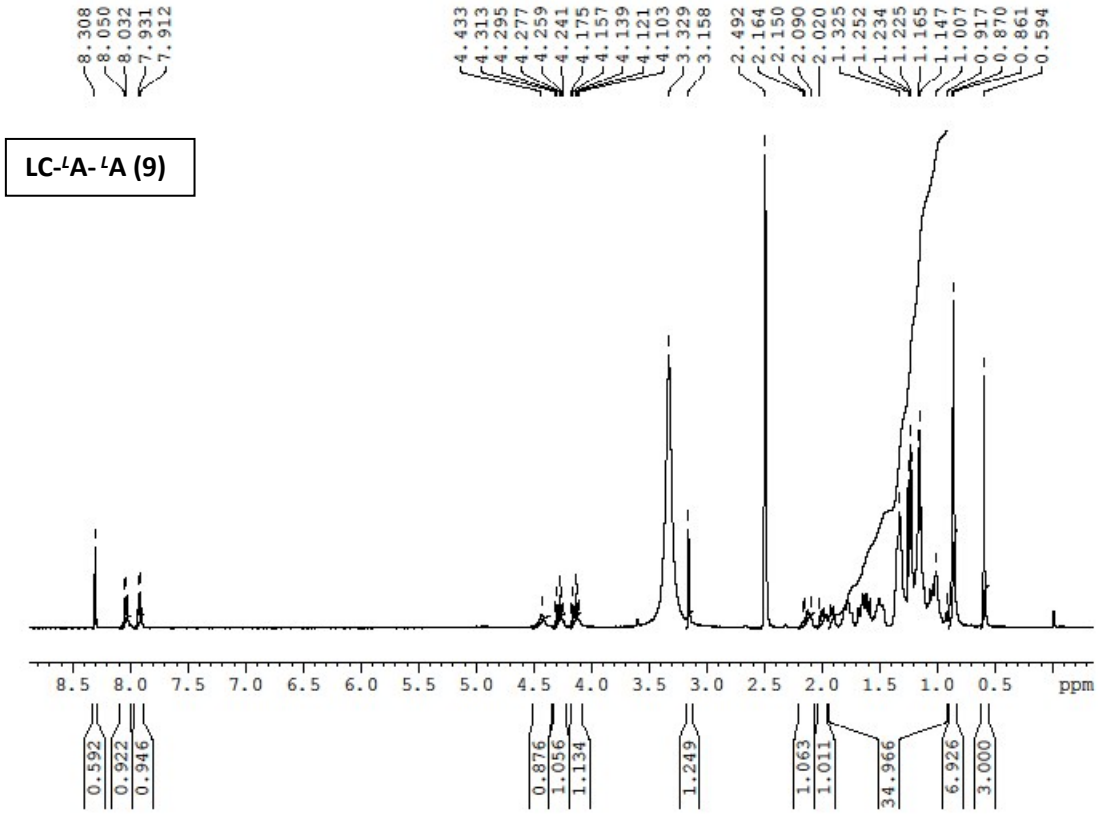

LC-DF-DF -OMe (8a)
173.452
171.237
170.662
136.404
135.610
129.279
129.123
128.495
128.480
127.033
126.884
77.321
77.004
76.686
71.725
60.344
56.406
55.956
53.945
53.381
52.225
42.663
42.035
40.363
40.113
38.024
37.805
36.371
35.778
35.381
35.307
34.514
33.357
31.521
30.451
28.155
27.142
26.365
24.138
23.328
20.983
20.760
18.264
14.133
12.005
ppm

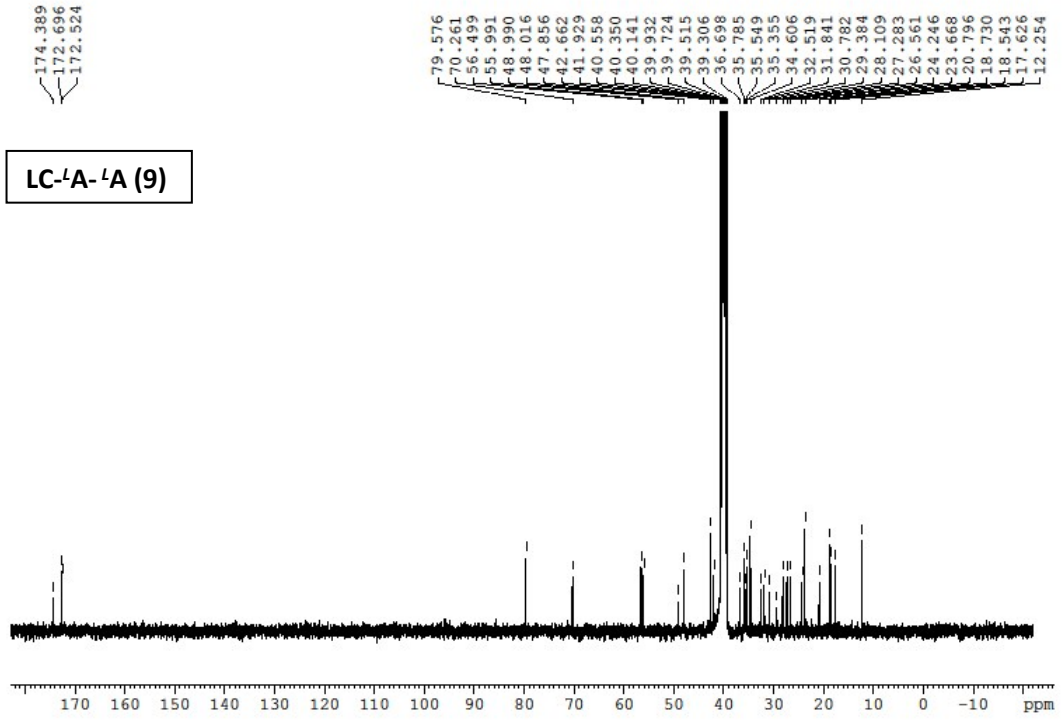

8.316
8.285
8.134
8.117
7.967
7.946
7.896
7.874
7.279
7.260
7.242
7.227
7.216
7.195
7.184
7.176
7.165
7.154
7.132
7.094
7.076
4.526
4.516
4.502
4.481
4.470
4.448
4.431
4.411
4.397
4.378
3.366
3.356
3.342
3.170
3.103
3.091
3.069
3.056
2.997
2.988
2.957
2.937
2.923
2.902
2.869
2.845
2.836
2.811
2.704
2.678
2.670
2.644
2.502
0.869
0.768
0.545
LC-DF-DF (8)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.43
0.70
0.72
0.23
9.96
2.44
0.41
1.36
2.16
1.00
3.33
3.03
3.00

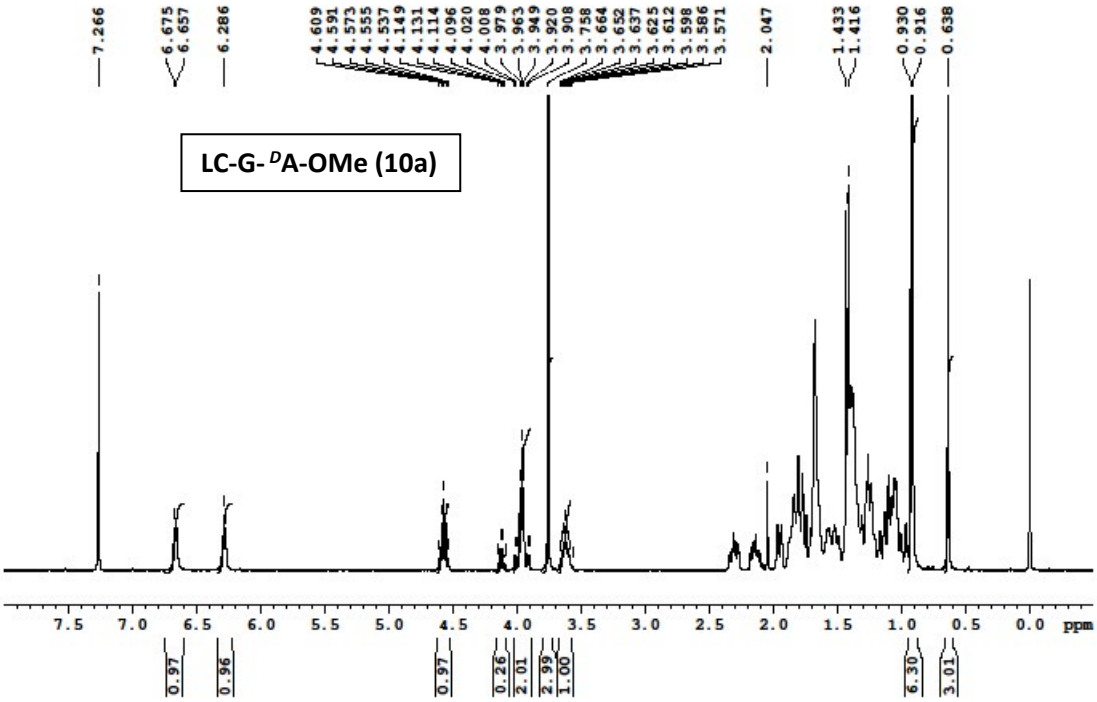

172.693
172.292
171.332
138.008
137.509
129.264
129.168
129.107
128.087
128.045
127.847
127.787
126.326
126.073
79.146
69.848
56.041
55.686
53.564
53.508
42.196
41.510
40.125
39.917
39.708
39.499
39.291
39.082
38.873
37.329
36.677
36.267
35.347
35.128
34.718
34.178
32.128
31.282
30.352
27.613
26.864
26.125
23.790
23.247
20.374
18.139
11.839
LC-DF-DF (8)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

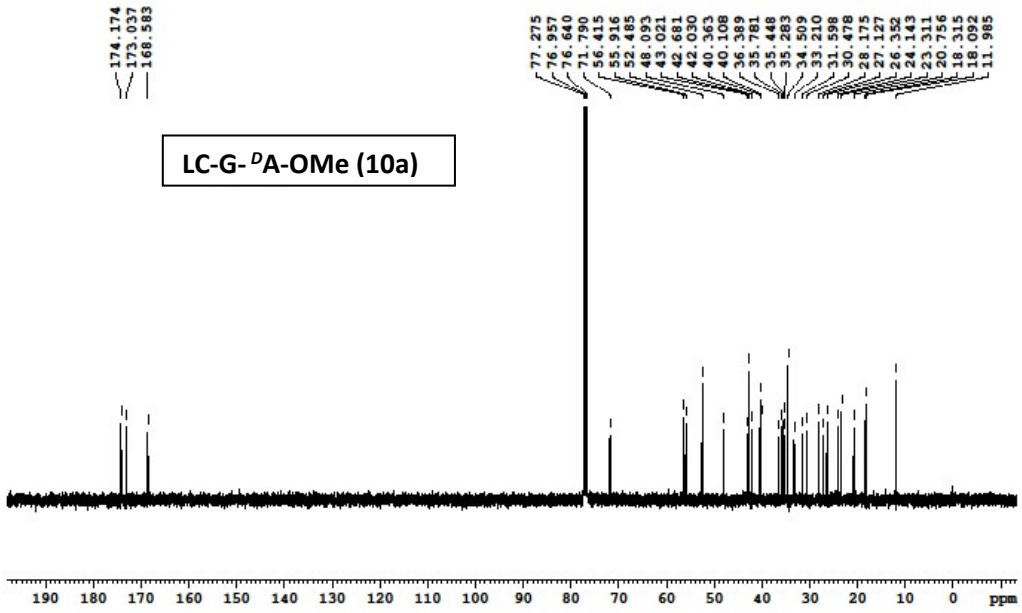

7.278
7.041
7.023
6.380
6.361
4.608
4.590
4.572
4.554
4.549
4.530
4.512
4.494
3.749
3.661
3.584
2.304
2.292
2.277
2.256
2.241
2.229
2.120
2.105
2.095
2.081
2.069
2.059
1.417
1.399
1.388
1.371
1.256
0.969
0.962
0.915
0.902
0.631
LC-LA-LA -OMe (9a)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.361
1.012
0.976
1.999
3.000
1.019
1.035
37.886
6.556
3.021

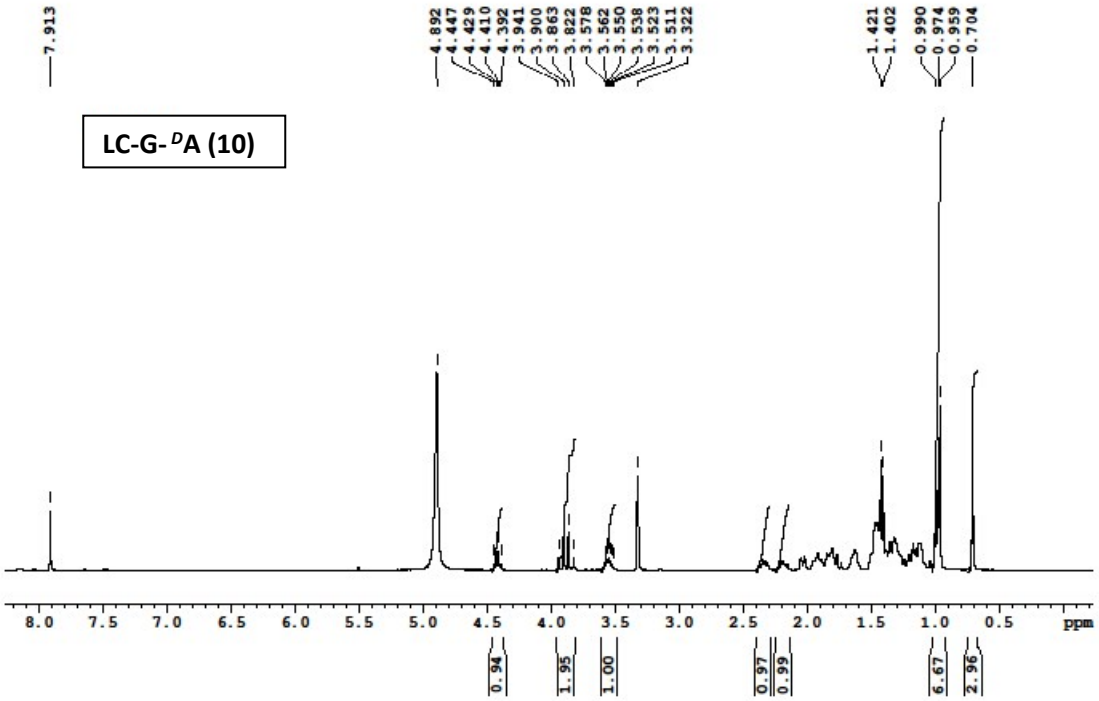

173.556
173.109
172.235
77.416
77.098
76.780
71.847
56.538
56.043
52.503
48.546
48.159
42.792
42.145
40.474
40.226
36.496
35.895
35.550
35.415
34.625
33.488
31.734
30.582
29.701
28.313
27.253
26.476
24.257
23.433
20.866
18.590
18.443
18.035
12.088
LC-LA-LA -OMe (9a)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

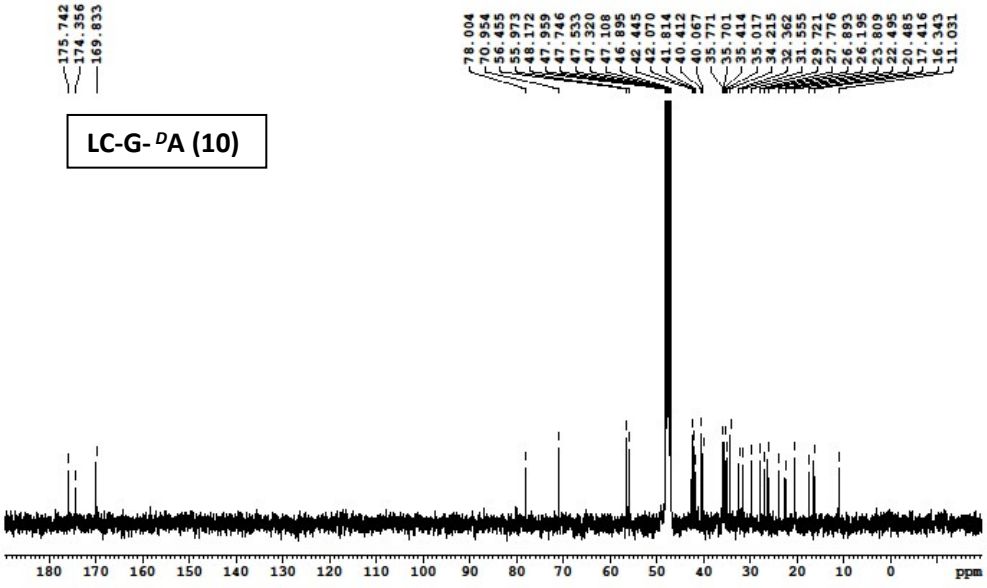

LC-ʟA-ʟA (9)
8.308
8.050
8.032
7.931
7.912
4.433
4.313
4.295
4.277
4.259
4.241
4.175
4.157
4.139
4.121
4.103
3.329
3.158
2.492
2.164
2.150
2.090
2.020
1.325
1.252
1.234
1.225
1.165
1.147
1.007
0.917
0.870
0.861
0.594
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.592
0.922
0.946
0.876
1.056
1.134
1.249
1.063
1.011
34.966
6.926
3.000


LC-ʟA-ʟA (9)
174.389
172.696
172.524
79.576
70.261
56.499
55.991
48.990
48.016
47.856
42.662
41.929
40.558
40.350
40.141
39.932
39.724
39.515
39.306
36.698
35.785
35.549
35.355
34.606
32.519
31.841
30.782
29.384
28.109
27.283
26.561
24.246
23.668
20.796
18.730
18.543
17.626
12.254
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


7.266
6.675
6.657
6.286
4.609
4.591
4.573
4.555
4.537
4.149
4.131
4.114
4.096
4.020
4.008
3.979
3.963
3.949
3.920
3.908
3.758
3.664
3.652
3.637
3.625
3.612
3.598
3.586
3.571
2.047
1.433
1.416
0.930
0.916
0.638
LC-G-DA-OMe (10a)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.97
0.96
0.97
0.26
2.01
2.99
1.00
6.30
3.01


174.174
173.037
168.583
77.275
76.957
76.640
71.790
56.415
55.916
52.485
48.093
43.021
42.681
42.030
40.363
40.108
36.389
35.781
35.448
35.283
34.509
33.210
31.598
30.478
28.175
27.127
26.352
24.143
23.311
20.756
18.315
18.092
11.985
LC-G-DA-OMe (10a)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


LC-G-^{D}A (10)
7.913
4.892
4.447
4.429
4.410
4.392
3.941
3.900
3.863
3.822
3.578
3.562
3.550
3.538
3.523
3.511
3.322
1.421
1.402
0.990
0.974
0.959
0.704
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.94
1.95
1.00
0.97
0.99
6.67
2.96


LC-G-^{D}A (10)
175.742
174.356
169.833
78.004
70.954
56.455
55.973
48.172
47.959
47.746
47.533
47.320
47.108
46.895
42.445
42.070
41.814
40.412
40.067
35.771
35.701
35.414
35.017
34.215
32.362
31.555
29.721
27.776
26.893
26.195
23.809
22.495
20.485
17.416
16.343
11.031
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm