

Supporting Information

Intra- and intermolecular hydrogen bonds enhance the fluoride-responsiveness of functionalized glycolipid-based gelators†

Cheng-Che Tsai,^a Wei-Tsung Chuang,^{*b} Yow-Fu Tsai,^{*a} Jyun-Ting Li,^a Yu-Fa Wu,^a
and Chun-Chen Liao^a

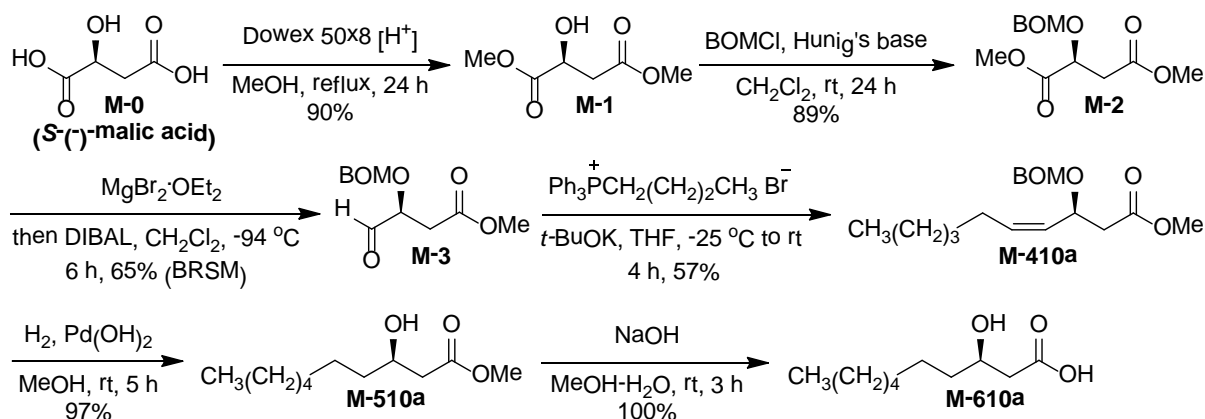
^a *Department of Chemistry, Chung Yuan Christian University, Chung Li 32023, Taiwan.*

E-mail: tsaiyofu@cycu.edu.tw

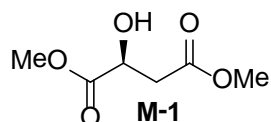
^b *National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan. E-mail: weitsung@nsrrc.org.tw*

Experimental Procedures

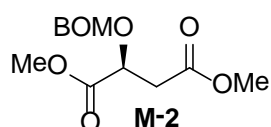
Synthesis of Optically Active (3*R*)-(+)-3-Hydroxydecanoic acid **M-610a**



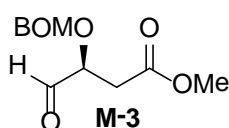
Scheme S1. Synthesis of Optically Active (3*R*)-(+)-3-hydroxydecanoic acid **M-610a**



(S)-(-)-2-Hydroxybutanic acid dimethyl ester (M-1). *S*-(-)-malic acid **M-0** (17.796 g, 133.00 mmol) and Dowex 50w X 8 [H⁺] (4 g) were added to a dried round-bottomed flask which was equipped an addition funnel contained 3Å molecular sieves and anhydrous MeOH (80.0 mL) was added. The resulting suspension solution was heated at reflux under N₂ for 18 h. The mixture was filtered to remove the resin and the filter was washed with MeOH. The crude yellow liquid was purified by distillation under reduced pressure (82 °C/0.2 mmHg) to give 19.636 g of **M-1** as a colorless liquid in 90% yield: $[\alpha]_D^{21} +2.3$ (c 10.2, CHCl₃); FT-IR (neat) ν_{\max} 3476, 2957, 1738, 1443 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.48 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.21 (d, *J* = 5.6 Hz, 1H, OH), 2.84 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.78 (dd, *J* = 16.4, 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.7 (C), 171.0 (C), 67.2 (CH), 52.9 (CH₃), 52.0 (CH₃), 38.4 (CH₂); HRMS-ESI HRMS-ESI [M + Na]⁺ Calcd for C₆H₁₀O₅Na 185.0426, Found 185.0426.

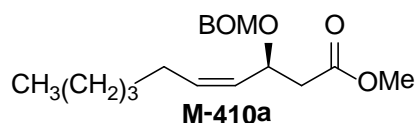


Dimethyl (2*S*)-2-((phenylmethoxy)methoxy)butanedioate (M-2). To a stirring solution of compound **M-1** (1.020 g, 6.30 mmol) in dry CH₂Cl₂ (7.9 mL) were added *N,N*-diisopropylethylamine (1.3 mL, 7.47 mmol), and benzyloxymethyl chloride, (1.8 mL, 12.60 mmol) at 0 °C. The mixture was warmed to room temperature and continuously stirred at this temperature. After 24 h, the reaction mixture was quenched with water, diluted with CH₂Cl₂, washed with brine, dried over MgSO₄, and concentrated in *vacuo*. Purification of the liquid crude product via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:4, v/v) observed 1.590 g of **M-2** as a colorless liquid in 88% yield: $R_f = 0.38$ (ethyl acetate – *n*-hexane, 1/4, v/v); $[\alpha]_D^{22} -38.9$ (c 0.20, CHCl₃); FT-IR (neat) ν_{\max} 2953, 2897, 1745, 1444, 1372, 1279, 1169, 1037, 743, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.26 (m, 5H), 4.86, 4.83 (ABq, $J = 7.2$ Hz, 2H), 4.63-4.60 (m, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 2.80 (d, $J = 6.0$ Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 171.7 (C), 170.4 (C), 137.5 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 94.5(CH₂), 71.9 (CH), 70.1 (CH₂), 52.3 (CH₃), 52.0 (CH₃), 37.6 (CH₂); HRMS-ESI [M + Na]⁺ Calcd for C₁₄H₁₈O₆Na 305.1001, Found 305.1006.



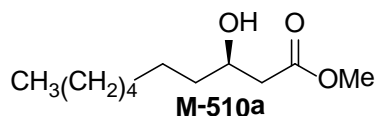
Methyl (3*S*)-4-oxo-3-((phenylmethoxy)methoxy)butanoate (M-3).¹ Powder MgBr₂ (2.220 g, 12.10 mmol) was added to a solution of compound **M-2** (2.040 g, 7.23 mmol) in dry CH₂Cl₂ (55.6 mL). The resulting mixture was stirred at room temperature for 1 h, and then cooled to –90 °C (acetone-liquid N₂), followed by treatment of a 1 M solution of diisobutylaluminum hydride in *n*-hexane (8.6 mL) with a 4 mL/h of rate. After the reaction mixture was stirred for 2 h at –90 °C, the reaction was quenched by adding dry MeOH (5.0 mL) at –90 °C and stirred for another 30 min at this temperature to destroy excess of diisobutylaluminum hydride. Saturated Rochelle salts (35.0 mL) was added to the resulting solution at –90 °C before the mixture was warmed to room temperature and continuously stirred for 2 h. The mixture was diluted with CH₂Cl₂, washed with brine, and dried over MgSO₄. The organic layer was removed the solvent, and then the colorless liquid residue was purified by flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:6, v/v) to afford 799 mg of **M-3** as a colorless liquid in 65% yield: $R_f = 0.38$ (ethyl

acetate:*n*-hexane = 1/4 (v/v)); $[\alpha]_D^{22} -16.3$ (c 0.15, CHCl₃); FT-IR (neat) ν_{\max} 3451, 2949, 2896, 1737, 1444, 1374, 1035, 742, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.28-7.34 (m, 5H), 4.89 (s, 2H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.36 (dd, *J* = 6.8, 4.4 Hz, 1H), 3.68 (s, 3H), 2.81 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.74 (dd, *J* = 16.4, 6.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 201.5 (CH), 170.5 (C), 137.1 (C), 128.5 (CH), 128.0 (CH), 127.9 (CH), 95.2 (CH₂), 78.7 (CH), 70.3 (CH₂), 52.1 (CH₃), 36.0 (CH₂); HRMS-ESI [M + Na]⁺ Calcd for C₁₃H₁₆O₅Na 275.0895, Found 275.0890.

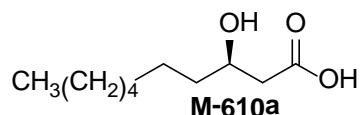


Methyl (3*S*,4*Z*)-3-((phenylmethoxy)methoxy)dec-4-enoate (M-410a). A suspension solution of hexyltriphenylphosphonium bromide (3.26 g, 9.09 mmol) in dry THF (2.3 mL) was treated with *t*-BuO⁻K⁺ (2.047 g, 18.18 mmol) at -25 °C. The mixture was stirred for 1 h at -25 °C, and then a solution of aldehyde **M-3** (1.01 g, 3.16 mmol) in dry THF (6.0 mL) was added to this resulting orange-red solution. After 1 h, the solution was warmed to room temperature and stirred for 3 h. The reaction was quenched by addition of cold saturated aqueous NH₄⁺Cl⁻ and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. Purification of the liquid crude product was performed by flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:20, v/v) to obtain 494 mg of colorless liquid **M-410a** as a *Z*-stereoisomer in 57% yield: *R*_f = 0.65 (ethyl acetate:*n*-hexane, 1/10 (v/v)); $[\alpha]_D^{28} -64.8$ (c 1.80, CHCl₃); FT-IR (neat) ν_{\max} 3007, 2957, 2932, 2860, 1744, 1497, 1456, 1437, 1373, 1283, 1250, 1200, 1172, 1097, 1036, 883, 829, 737, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.26 (m, 5H), 5.63 (dt, *J* = 11.1, 7.5 Hz, 1H), 5.23 (dd, *J* = 11.1, 9.3 Hz, 1H), 4.98-4.91 (m, 1H), 4.73 (d, *J* = 6.9 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 6.9 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.66 (s, 3H), 2.63 (dd, *J* = 15.0, 8.7 Hz, 1H), 2.45 (dd, *J* = 15.0, 5.1 Hz, 1H), 2.15-2.06 (m, 2H), 1.35-1.24 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.2 (C), 137.9 (C), 135.5 (CH), 128.3 (CH), 127.9 (CH), 127.6 (CH), 127.5 (CH), 91.2 (CH₂), 69.2 (CH₂), 67.6 (CH), 51.6 (CH₃), 40.9 (CH₂), 31.4 (CH₂), 29.2 (CH₂), 27.6 (CH₂), 22.4 (CH₂), 14.0 (CH₃); LCMS-ESI [M + Na]⁺ Calcd for C₁₉H₂₈O₄Na 343.20, Found 343.20; HRMS-ESI [M + H]⁺ Calcd for C₁₉H₂₉O₄Na

343.1880, Found 343.1896.

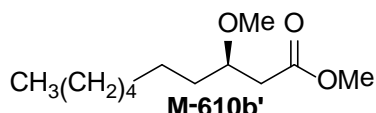


Methyl (3R)-3-hydroxydecanoate (M-510a). To a solution of compound **M-410a** (236 mg, 0.74 mmol) in MeOH (4 mL) was added Pd(OH)₂/C (24 mg). The mixture was stirred under hydrogen (50 psi) at room temperature for 5 h. The Pd/C was removed through a short pad of SiO₂/Celite and the filter was washed with CH₂Cl₂. The filtrate was concentrated in *vacuo*, and then the yellow liquid residue was purified via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:20 (v/v)) to furnish 145 mg of **M-510a** as a colorless liquid in 97% yield: R_f = 0.18 (ethyl acetate:*n*-hexane = 1:10 (v/v)); $[\alpha]_D^{28}$ -14.5 (c 1.20, CHCl₃) (lit. $[\alpha]_D^{20}$ -13.5 (c 2.5, CHCl₃)); FT-IR (neat) ν_{\max} 3460, 2957, 2932, 2856, 1734, 1437, 1369, 1288, 1261, 1198, 1165, 1126 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.00-3.95 (m, 1H), 3.69 (s, 3H), 2.87 (d, J = 4.0 Hz, 1H, OH), 2.49 (dd, J = 16.4, 3.2 Hz, 1H), 2.39 (dd, 1H, J = 16.4, 9.2Hz), 1.51-1.36 (m, 2H), 1.25 (brs, 10H), 0.87 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.5 (C), 68.0 (CH), 51.7 (CH₃), 41.1 (CH₂), 36.5 (CH₂), 31.8 (CH₂), 29.5 (CH₂), 29.2 (CH₂), 25.5 (CH₂), 22.6 (CH₂), 14.1 (CH₃); HRMS-ESI $[M + Na]^+$ Calcd for C₁₁H₂₂O₃Na 225.1461, Found 225.1468.

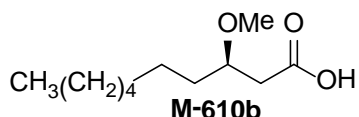


(3R)-(+)-3-hydroxydecanoic acid (M-610a). 1 N aqueous NaOH (10 equivalent) was slowly added to the solution of **M-510a** (150 mg, 0.74 mmol) in methanol (5 mL) at 0 °C. The reaction mixture was warmed to room temperature and continuously stirred at this temperature. After 3 h, the reaction mixture was acidified with Dowex 50w X 8 [H⁺] to pH 4 and then filtered to remove the resin. The filtrate was concentrated in *vacuo* to observe 140 mg of **M-610a** as a colorless syrup, which was used without further purification, in 100% yield: R_f = 0.5 (CH₂Cl₂:MeOH = 3:1 (v/v)); $[\alpha]_D^{28}$ +2.1 (c 0.95, MeOH); FT-IR (neat) ν_{\max} 3432, 2956, 2926, 2856, 1717, 1466, 1416, 1377, 1217, 1176, 1126, 1083, 1048 cm⁻¹; ¹H

NMR (400 MHz, CD₃OD) δ 3.99-3.94 (m, 1 H), 2.44 (dd, $J = 15.3, 4.8$ Hz, 1H), 2.37 (dd, $J = 15.3, 8.2$ Hz, 1H), 1.49-1.45 (m, 2 H), 1.32 (brs, 10 H), 0.90 (d, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 176.0 (C), 69.6 (CH), 43.5 (CH₂), 38.4 (CH₂), 33.3 (CH₂), 30.9 (CH₂), 30.7 (CH₂), 27.0 (CH₂), 24.0 (CH₂), 14.7 (CH₃); HRMS-ESI [M + Na]⁺ Calcd for C₁₀H₂₀O₃Na 211.1305, Found 211.1313.



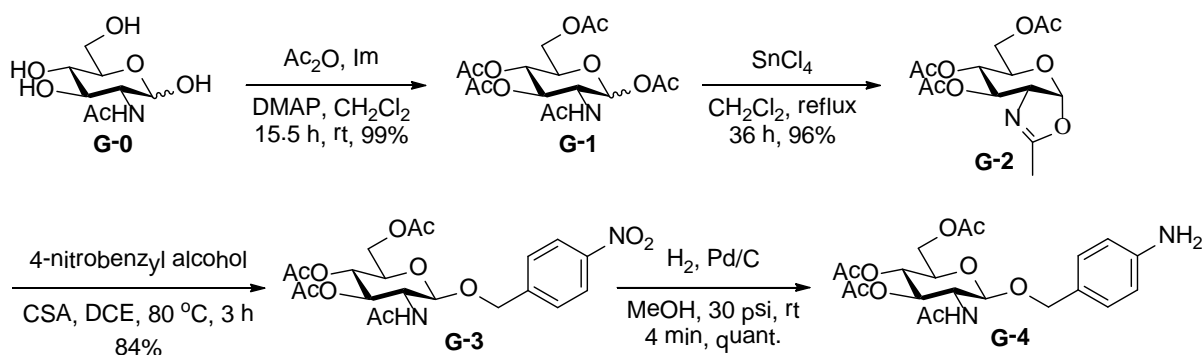
Methyl (R)-3-methoxydecanoate (M-610b'). A solution of hydroxyl ester **M-510a** (57 mg, 0.28 mmol) in dry DMF (0.9 mL, 0.3 M) was treated with NaH (45 mg, 1.13 mmol) at 0 °C. After 15 min, the methyl iodide (0.4 mL, 64 mmol) was added at the same temperature and then continuously stirred at room temperature for 8 h. The reaction mixture was neutralized with Dowex 50w X 8 [H⁺], filtered and concentrated under reduced pressure to give a yellow solid residue. Purification of the residue was performed by flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:40, v/v) to get 45 mg of colorless liquid **M-610b'** in 74% yield: $R_f = 0.5$ (EtOAc/*n*-hexane = 1:10 (v/v)); $[\alpha]_D^{28} -4.1$ (c 1.24, CHCl₃); FT-IR (neat) ν_{\max} 3456, 2928, 2856, 1742, 1460, 1437, 1369, 1314, 1245, 1199, 1164, 1100, 1014 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.66 (s, 1H), 3.63-3.57 (m, 1H), 3.32 (s, 3H), 2.50 (dd, $J = 15.2, 7.6$ Hz, 1H), 2.39 (dd, $J = 15.2, 5.2$ Hz, 1H), 1.53-1.42 (m, 2H), 1.41 (brs, 10H), 0.85 (t, $J = 6.8$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.3 (C), 77.3 (CH), 56.9 (CH₃), 51.5 (CH₃), 39.2 (CH₂), 33.8 (CH₂), 31.7 (CH₂), 29.6 (CH₂), 29.2 (CH₂), 25.0 (CH₂), 22.6 (CH₂), 14.0 (CH₃); HRMS-ESI [M + Na]⁺ Calcd for C₁₂H₂₄O₃Na 239.1618, Found 239.1618.



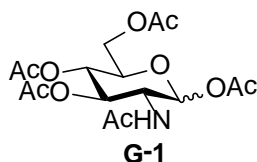
Methyl (R)-3-methoxydecanoic acid (M-610b). 65 mg of acid compound **M-610b** was afforded in 100% yield from ester **M-610b'** (70 mg, 0.32 mmol) according to the procedure of preparing acid compound **M-610a**: $R_f = 0.4$ (CH₂Cl₂:MeOH = 10:1 (v/v)); $[\alpha]_D^{27} +3.0$ (c 0.67, MeOH); FT-IR (neat) ν_{\max} 3442,

2928, 2857, 2670, 1712, 1460, 1412, 1378, 1294, 1222, 1184, 1099, 952, 840 cm^{-1} ; ^1H NMR (400 MHz, CD_3OD) δ 3.67-3.61 (m, 1H), 3.35 (s, 3H), 2.47 (dd, $J = 14.5$, 6.8 Hz, 1H), 2.32 (dd, $J = 14.5$, 5.8 Hz, 1H), 1.53-1.50 (m, 2H), 1.31 (brs, 10H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 177.7 (C), 80.1 (CH), 57.4 (CH_3), 35.4 (CH_2), 33.3 (CH_2), 31.1 (CH_2), 30.7 (CH_2), 26.6 (CH_2), 24.0 (CH_2), 14.7 (CH_3); HRMS-ESI $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_3\text{Na}$ 225.1467, Found 225.1473.

Synthesis of *p*-Aminobenzyl β -2-acetamido-2-deoxy-D-glucopyranoside **G-4**

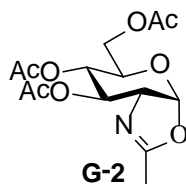


Scheme S2. Synthesis of *p*-Aminobenzyl β -D-glucopyranoside **G-4**



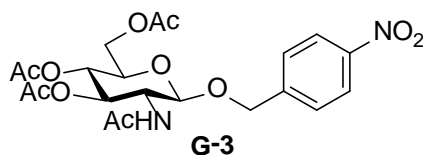
2-Acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-D-glucopyranose (G-1). To a stirred suspension solution of D-glucosamine (**G-0**) (0.500 g, 2.26 mmol), imidazole (0.924 g, 13.59 mmol), and DMAP (0.028 mg, 0.23 mmol) in dry CH_2Cl_2 (10 mL) was slowly added the acetic anhydride (1.9 mL, 0.02 mol) at 0°C . After 10 min at 0°C , the resulting solution was allowed to stir at room temperature for another 24 h. After completion of acetylation, the reaction mixture was dilute with CH_2Cl_2 and successively washed with 1 N or 2 N cold HCl, saturated aqueous NaHCO_3 , and brine. The organic layer was dried over MgSO_4 and concentrated under reduced pressure without further purification to give 841 mg of a white powder acetate **G-1** as a ca. 4.6:1.0 mixture of α - and β -stereoisomers in 82% yield: $R_f = 0.25$ (ethyl acetate:*n*-hexane = 4:1 (v/v)); FT-IR (neat) ν_{max} 3255, 3072, 3000, 2952, 2924, 1743, 1675, 1519, 1429, 1382, 1302, 1242, 1130, 1099, 1040, 944

cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) α -isomer: δ 6.17 (d, $J = 3.7$ Hz, 1H), 5.54 (d, $J = 9.0$ Hz, 1H), 5.26-5.19 (m, 2H), 4.51-4.46 (m, 1H), 4.32-4.23 (m, 1H), 4.07 (dd, $J = 2.5, 12.5$ Hz, 1H), 4.01-3.97 (m, 1H), 2.19 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.94 (s, 3H); β -isomer: δ 5.69 (d, $J = 8.8$ Hz, 1H), 5.49 (d, $J = 9.6$ Hz, 1H), 5.16-5.09 (m, 2H), 4.51-4.46 (m, 1H), 4.32-4.23 (m, 1H), 4.13 (dd, $J = 2.4, 12.5$ Hz, 1H), 3.80-3.77 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.6 (C), 171.0 (C), 170.6 (C), 170.1 (C), 169.9 (CH), 169.4 (C), 169.2 (C), 169.0 (C), 168.6 (C), 92.5 (CH), 90.6 (CH), 72.7 (CH), 72.5 (CH), 70.6 (CH), 69.6 (CH), 67.7 (CH), 67.4 (CH), 61.6 (CH_2), 61.4 (CH_2), 52.8 (CH), 50.9 (CH), 23.1 (CH_3), 22.9 (CH_3), 20.9 (CH_3), 20.6 ($\text{CH}_3 \times 2$), 20.5 (CH_3); HRMS-ESI $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_{10}\text{Na}$ 412.1214, Found 412.1228.

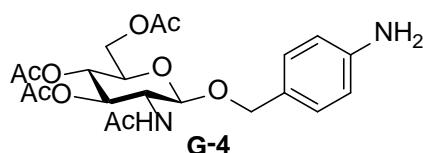


2-Methyl-(3,4,6-tri-O-acetyl-1,2-dideoxy- α -D-glucopyrano)-[2,1-d]-2-oxazoline (G-2).³ After the acetate **G-1** (0.500 g, 1.28 mmol) was completely dissolved in dry CH_2Cl_2 (8.5 mL, 0.15 M), freshly distilled stannic chloride (IV) (0.17 mL, 1.41 mmol) was added at 0 °C and then the reaction mixture was heated at reflux for 36 h. After starting material being consumed, the reaction mixture was diluted with dry CH_2Cl_2 and made slightly alkaline with saturated aqueous NaHCO_3 at 0 °C. The separated aqueous layer was extracted with CH_2Cl_2 and then the combined organic layer was washed with brine to pH 7.0, dried over MgSO_4 , and concentrated in vacuo. The produced yellow syrup was purified by flash column chromatography on silica gel using ethyl acetate and *n*-hexane (4:1 (v/v)) as the eluent to give 0.407 g of oxazoline **G-2** as a colorless syrup in 96% yield: $R_f = 0.25$ (ethyl acetate:*n*-hexane = 1:4 (v/v)); $[\alpha]_D^{24} +26.9$ (c 0.24, CHCl_3) (lit. $[\alpha]_D^{22} + 17.2$ (c 1.60, CHCl_3)); FT-IR (neat) ν_{max} 2957, 2928, 2854, 1746, 1673, 1437, 1370, 1316, 1234, 1132, 1099, 1039, 942, 900, 734 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.94 (d, $J = 7.2$ Hz, 1H), 5.26 (dd, $J = 8.0, 2.0$ Hz, 1H), 4.91 (d, $J = 8.0$ Hz, 1H), 4.16 (d, $J = 4.8$ Hz, 2H), 4.11 (d, $J = 6.0$ Hz, 1H), 3.61-3.57 (m, 1H), 2.09, 2.07 $\times 2$, 2.06 (each s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5 (C), 169.4 (C), 169.1 (C), 166.9 (C), 99.3 (CH), 70.0 (CH), 68.1 (CH), 67.4 (CH), 64.5 (CH), 63.2 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3),

13.7 (CH₃); HRMS-ESI [M + Na]⁺ Calcd for C₁₄H₁₉NO₈Na 352.1003, Found 352.0998.



***p*-Nitrobenzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (G-3).**⁴ To a solution of oxazoline **G-2** (30 mg, 0.09 mmol) and 4-nitrobenzyl alcohol (3 mg, 0.01 mmol) in dry 1,2-dichloroethane (DCE, 0.43 mL, 0.21 M) was added a catalytic amount of (\pm)-10-camphorsulfonic acid (CSA, 2 mg, 0.01 mmol). The reaction mixture was then refluxed for 2.5 h. The reaction mixture was then neutralized with anhydrous Et₃N at 0 °C and washed with saturated aqueous NaHCO₃, brine, dried with over MgSO₄, filtered and evaporated under reduced pressure to give a brown solid residue. The residue was chromatographed on a silica gel column (ethyl acetate:*n*-hexane = 4:1 (v/v)) to obtain 37 mg of the product **G-3** as a white solid compound in 84% yield: *R*_f = 0.25 (ethyl acetate:*n*-hexane = 4:1 (v/v)); mp = 182-183 °C; [α]_D³⁰ -54.5 (c 2.00, CHCl₃); FT-IR (neat) ν_{\max} 3297, 3112, 3074, 2945, 2881, 1744, 1663, 1603, 1520, 1377, 1347, 1236, 1113, 1086, 1048, 903, 858, 843, 795, 738 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 6.05 (brs, 1H), 5.25 (dd, *J* = 10.5, 9.6 Hz, 1H), 5.07 (t, *J* = 9.6 Hz, 1H), 4.96, 4.68 (ABq, *J* = 13.4 Hz, 1H), 4.76 (d, *J* = 8.4 Hz, 1H), 4.24 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.01 (dd, *J* = 10.5, 8.4 Hz, 1H), 3.73 (ddd, *J* = 9.9, 4.5, 2.1 Hz, 1H), 2.05, 2.00, 1.99, 1.92 (each s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 170.7 (C), 170.5 (C), 170.3 (C), 169.3 (C), 147.2 (C), 144.8 (C), 127.6 (CH), 123.4 (CH), 100.2 (CH), 72.1 (CH), 71.9 (CH), 69.2 (CH₂), 68.5 (CH), 62.0 (CH₂), 54.3 (CH), 23.1 (CH₃), 20.6 (CH₃), 20.5 (CH₃×2); HRMS (ESI) Calcd for C₂₁H₂₆N₂ONa 505.1429, Found 505.1424



***p*-Aminobenzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranoside (G-4).** To a solution of **G-3** (100 mg, 0.21 mmole) in 4.1 mL of methanol at room temperature was added activated 10% Pd/C (22 mg). The reaction mixture was

stirred for 3 min. under a hydrogen atmosphere (30 psi) at the same temperature. After the reaction was complete, monitored by TLC, it was filtered through a short pad of Celite and the Celite pad was washed with ethyl acetate. The filtrate obtained was concentrated in vacuo without further purification to yield 94 mg of saturated ester **7** as a brown solid compound in 99% yield: $R_f = 0.18$ (ethyl acetate:*n*-hexane = 4:1 (v/v)); mp = 149-150 °C; $[\alpha]_D^{30} -49.1$ (c 2.02, CHCl₃); FT-IR (neat) ν_{\max} 3368, 3293, 3065, 2954, 2881, 1748, 1663, 1542, 1521, 1433, 1370, 1234, 1122, 1044, 905, 831, 735, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.06 (d, $J = 8.1$ Hz, 2H), 6.63 (d, $J = 8.1$ Hz, 2H), 5.30 (d, $J = 9.0$ Hz, 1H), 5.14 (dd, $J = 10.2, 9.3$ Hz, 1H), 5.05 (t, $J = 9.3$ Hz, 1H), 4.74 (d, $J = 11.7$ Hz, 1H), 4.54 (d, $J = 8.7$ Hz, 1H), 4.46 (d, $J = 11.7$ Hz, 1H), 4.25 (dd, $J = 12.2, 4.7$ Hz, 1H), 4.14 (dd, $J = 12.2, 2.1$ Hz, 1H), 3.91 (dd, $J = 10.2, 8.7$ Hz, 1H), 3.61 (ddd, $J = 9.3, 4.7, 2.1$ Hz, 1H), 2.09, 1.99, 1.87 (each s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9(C), 170.7 (C), 170.1 (C), 169.4 (C), 146.5 (C), 129.9 (CH), 126.3 (C), 114.9 (CH), 98.7 (CH), 72.5 (CH), 71.7(CH), 70.5 (CH₂), 68.7 (CH), 62.2 (CH₂), 54.4 (CH), 23.2 (CH₃), 20.7 (CH₃), 20.6 (CH₃×2); HRMS-ESI [M + Na]⁺ Calcd for C₂₁H₂₈N₂O₉Na 475.1687, Found 475.1682.

References:

1. G. E. Keck, M. B. Andrus and D. R. Romer, *J. Org. Chem.*, 1991, **56**, 417.
2. (a) D. Heseck, M. Suvorov, K-i. Morio, M. Lee, S. Brown, S. B. Vakulenko and S. Mobashery, *J. Org. Chem.*, 2004, **69**, 778; (b) V. Y. Smastava, *Carbohydr. Res.*, 1982, **103**, 286.
3. K. Yamada, E. Fujita, S.-I. Nishimura, *Carbohydr. Res.*, 1998, **305**, 443.

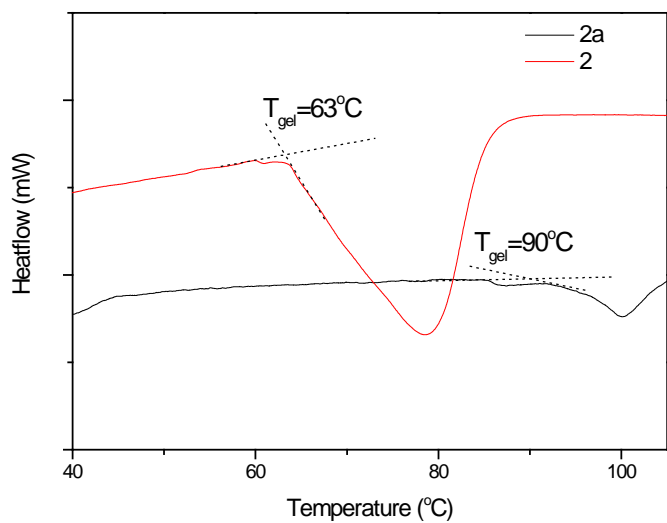


Figure S1. DSC thermograms of gelators 2 and 2a (heating rate 10°C/min)

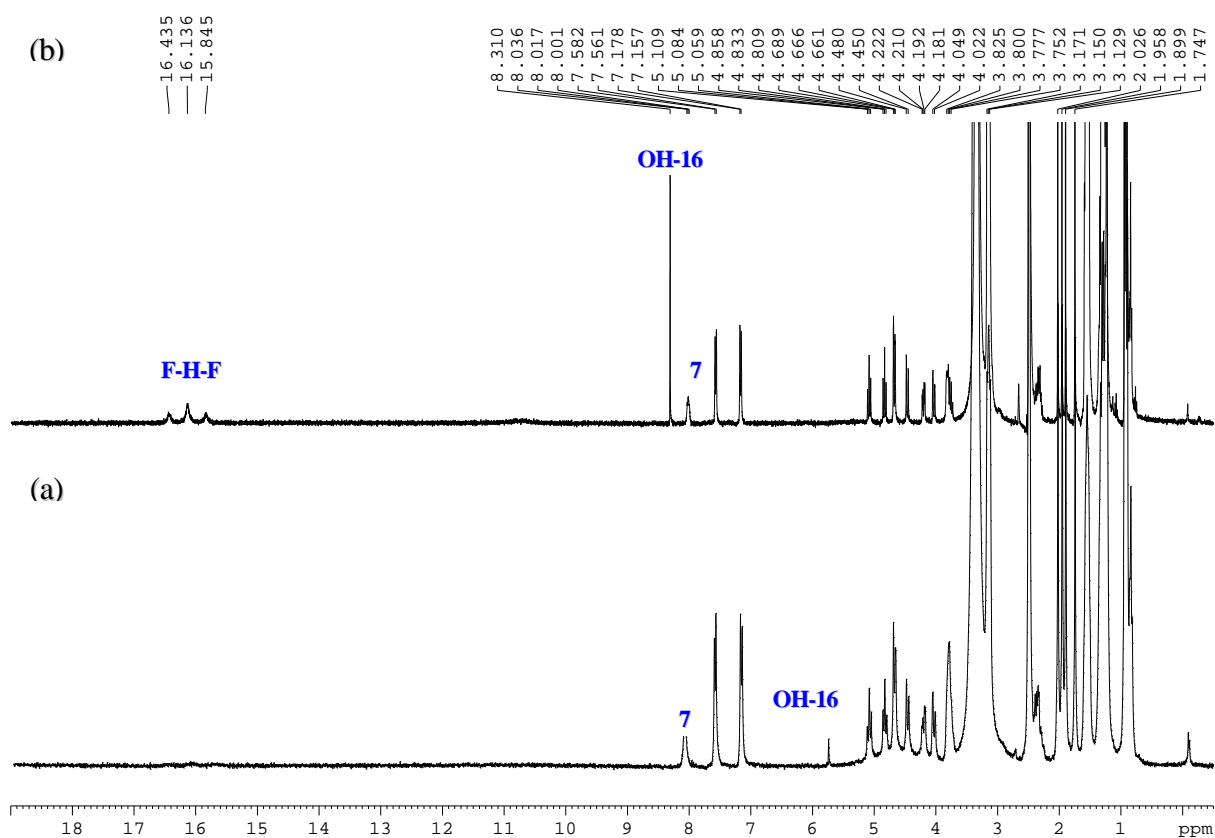
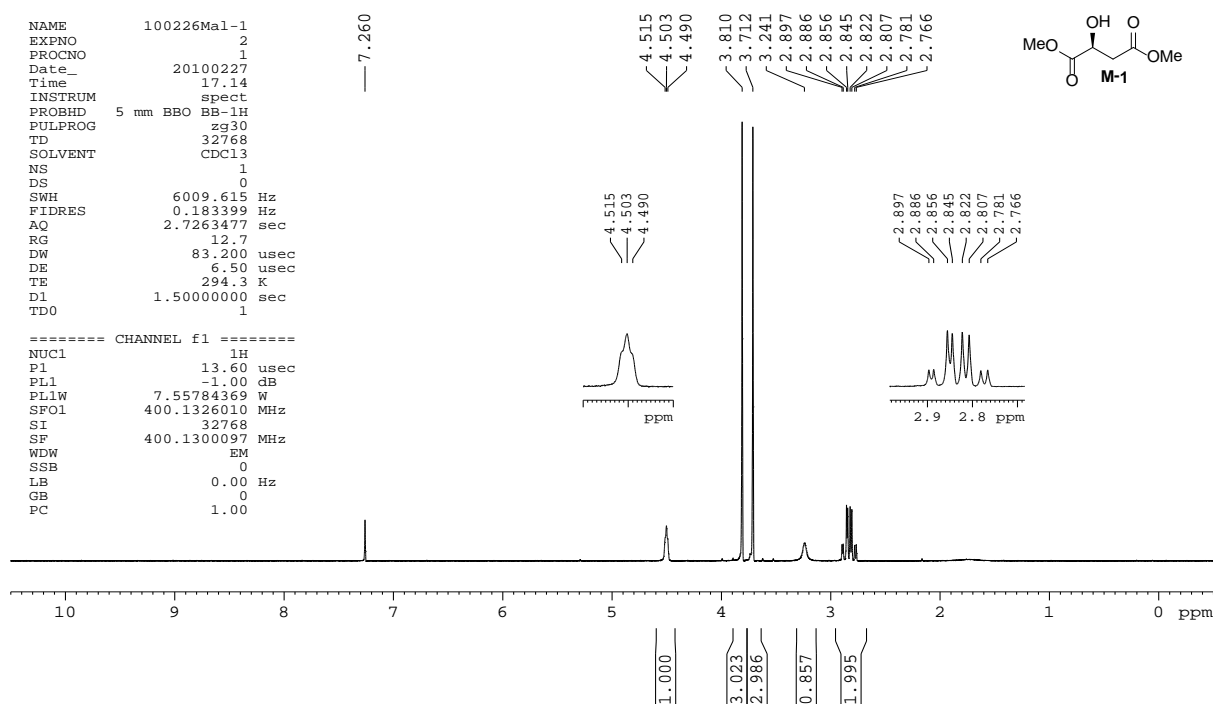
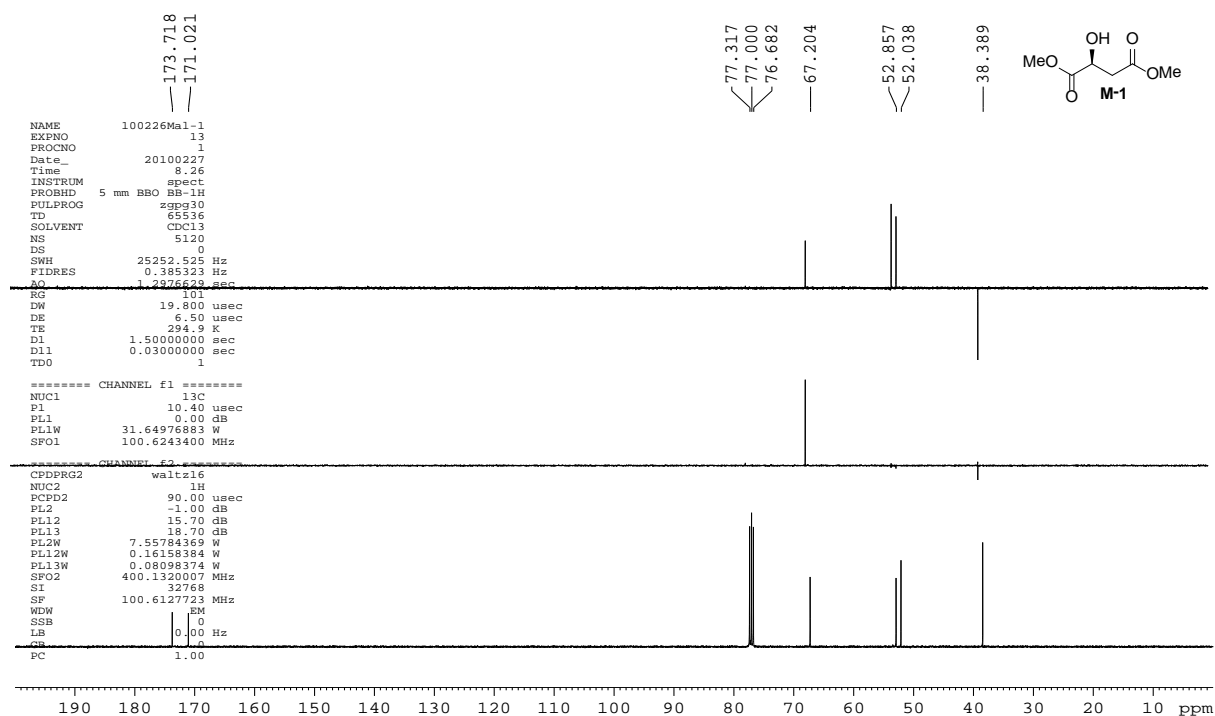


Fig. S1 ^1H NMR spectra of gelator **2a** (10 mM) in $\text{DMSO-}d_6$ upon the addition of F^- . (a) 1 equiv. of F^- , (b) 5 equiv. of F^- .

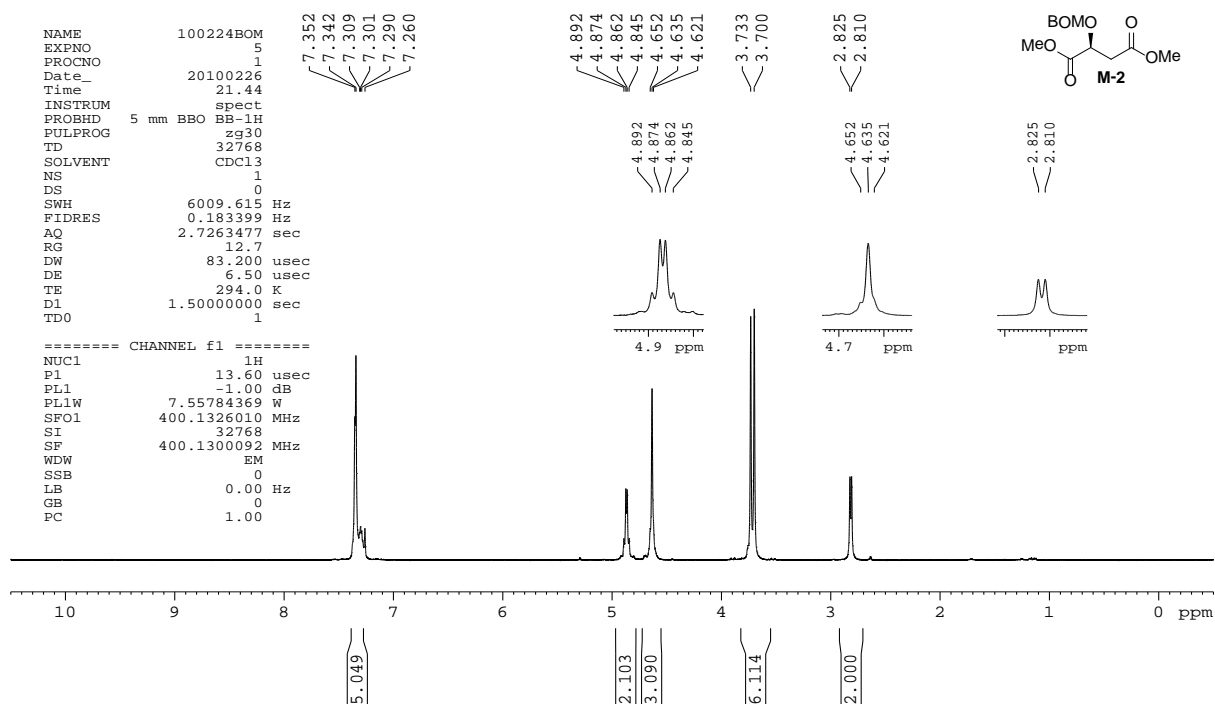
¹H NMR Spectrum of Compound M-1



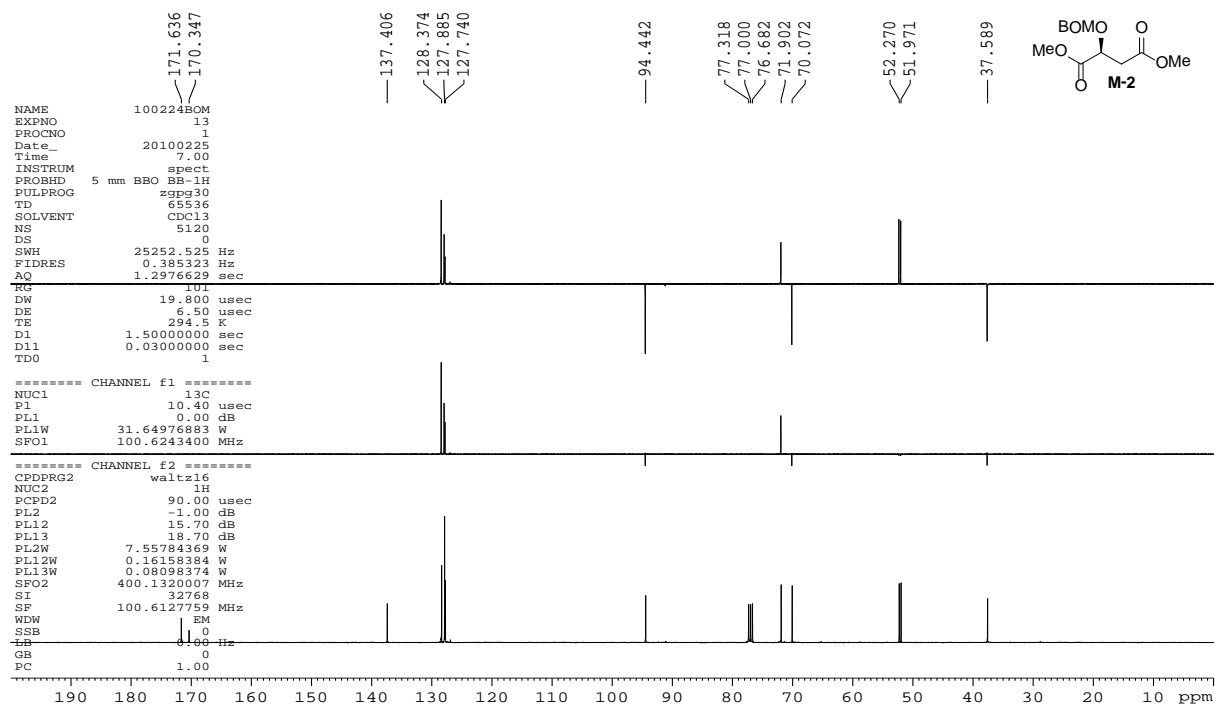
¹³C and DEPT NMR Spectrum of Compound M-1



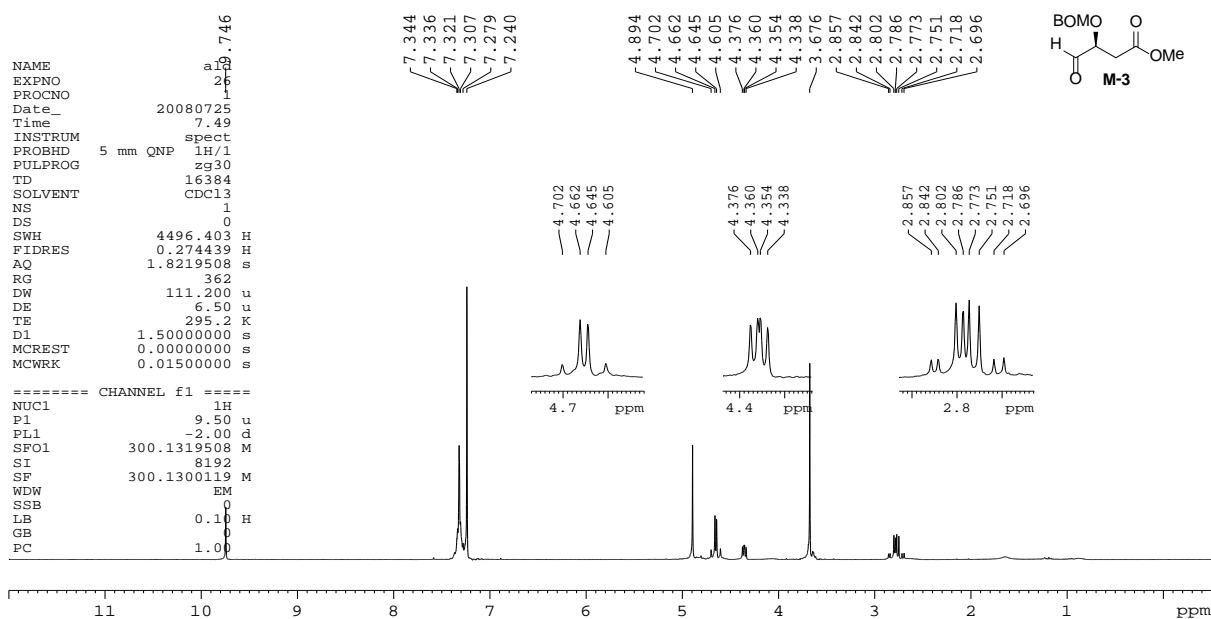
¹H NMR Spectrum of Compound M-2



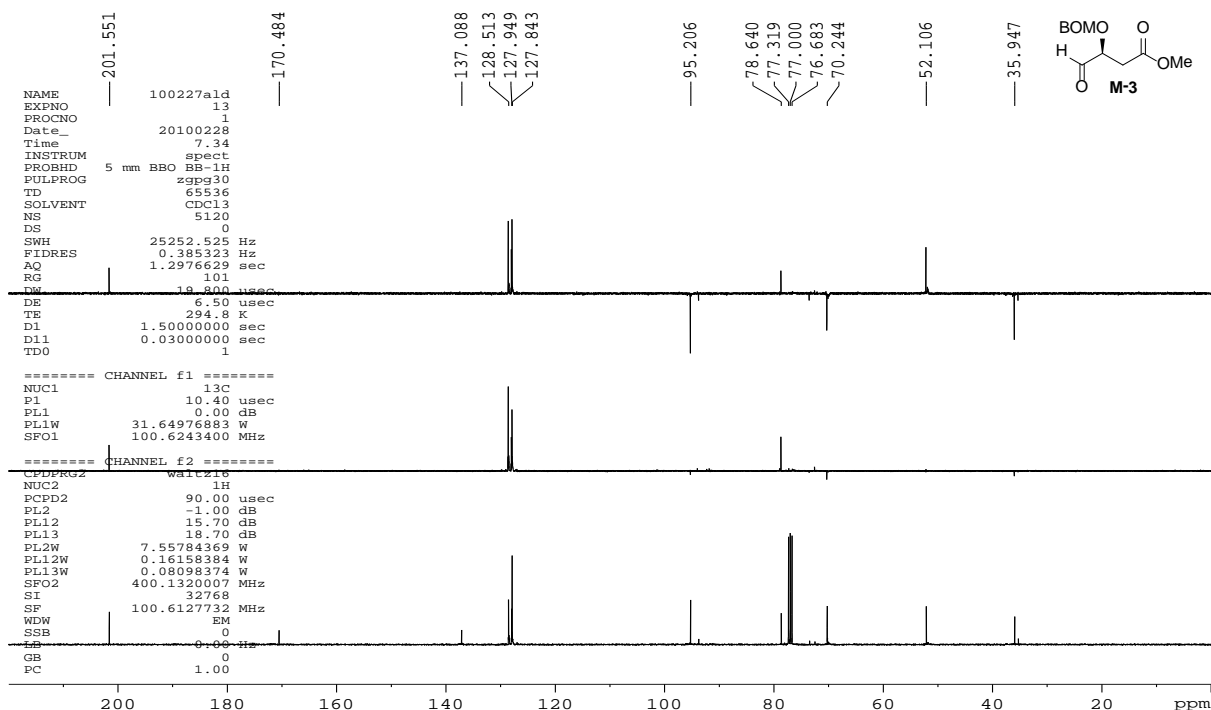
¹³C and DEPT NMR Spectrum of Compound M-2



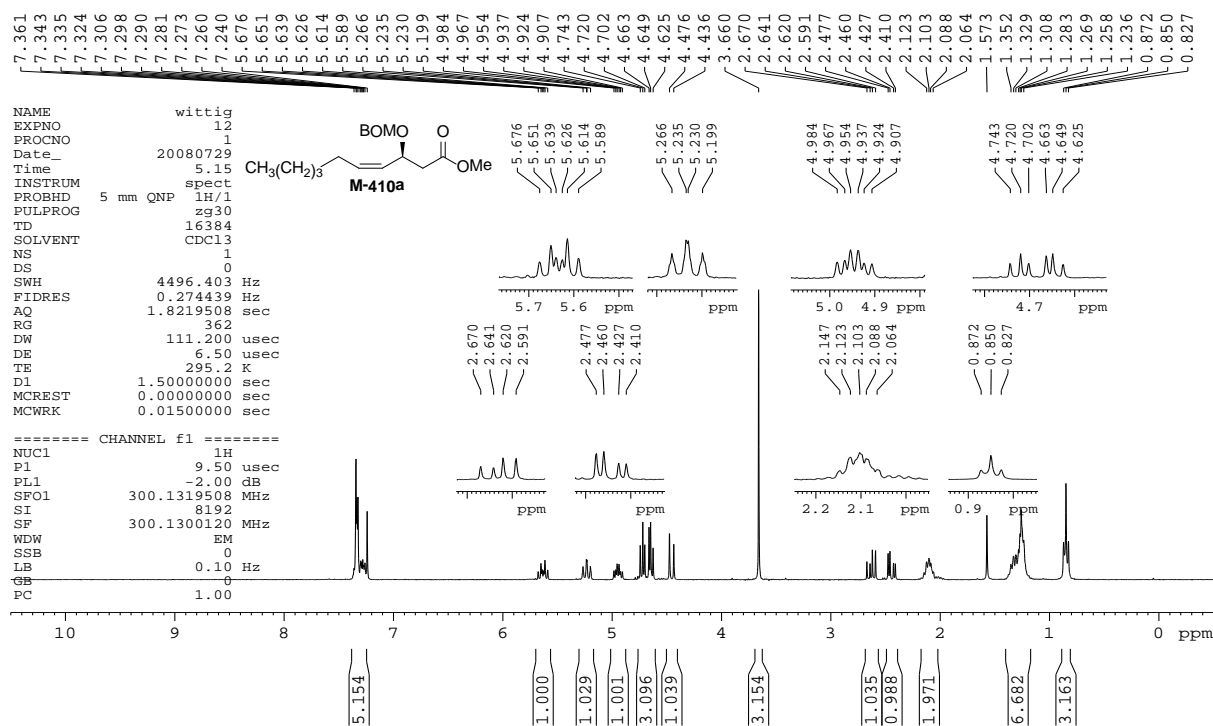
¹H NMR Spectrum of Compound M-3



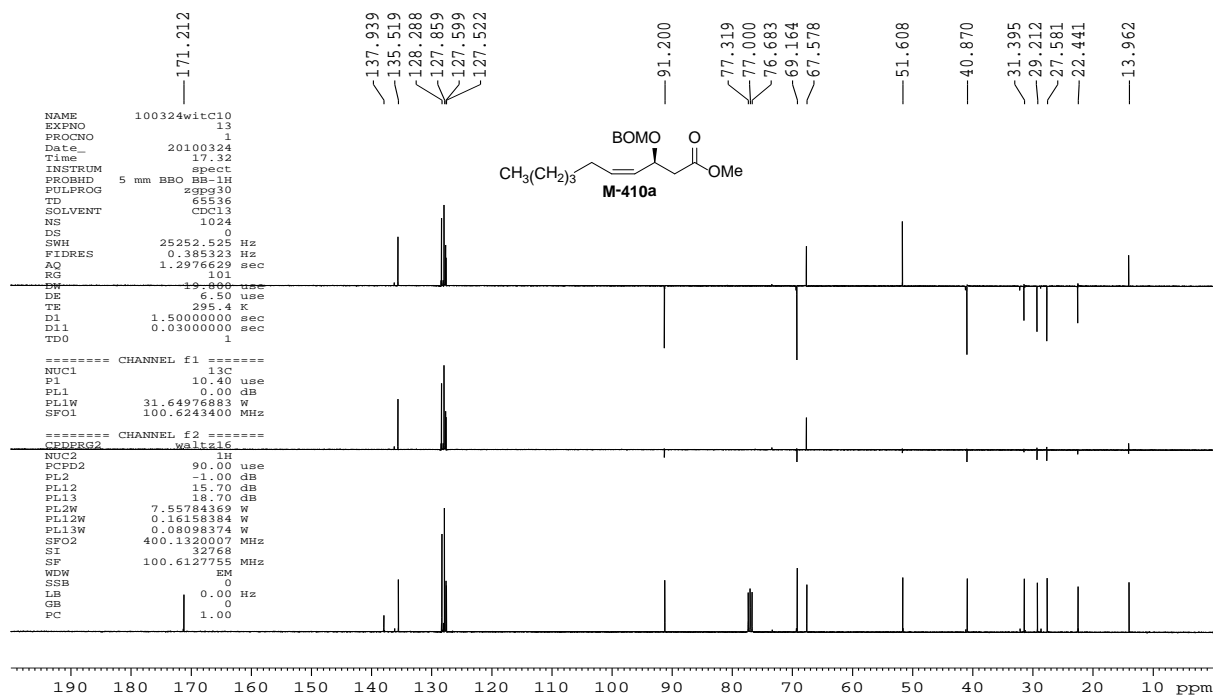
¹³C and DEPT NMR Spectrum of Compound M-3



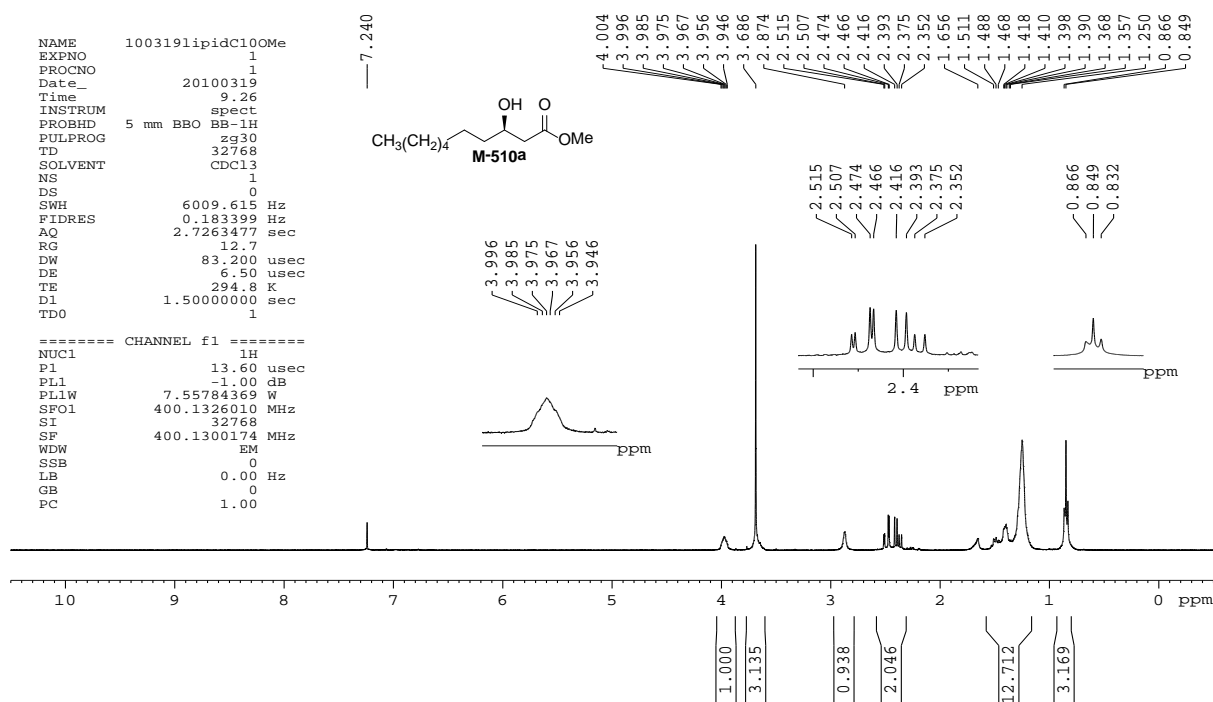
¹H NMR Spectrum of Compound M-410a



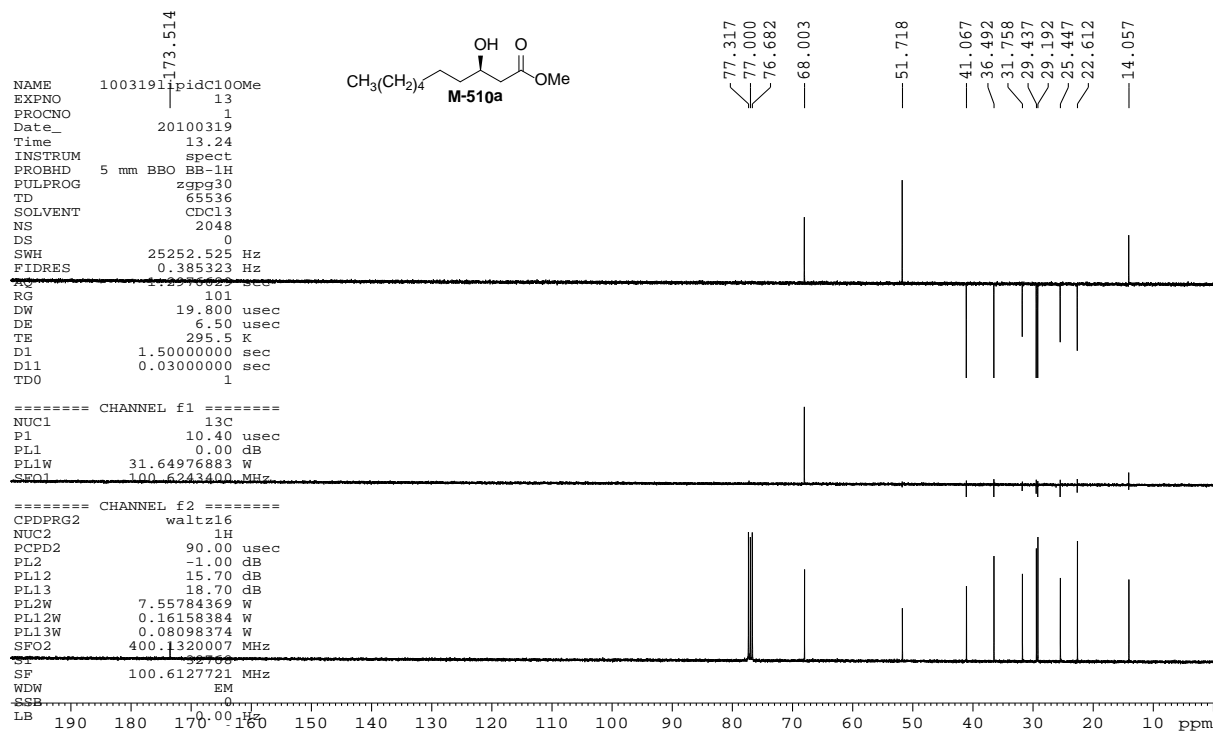
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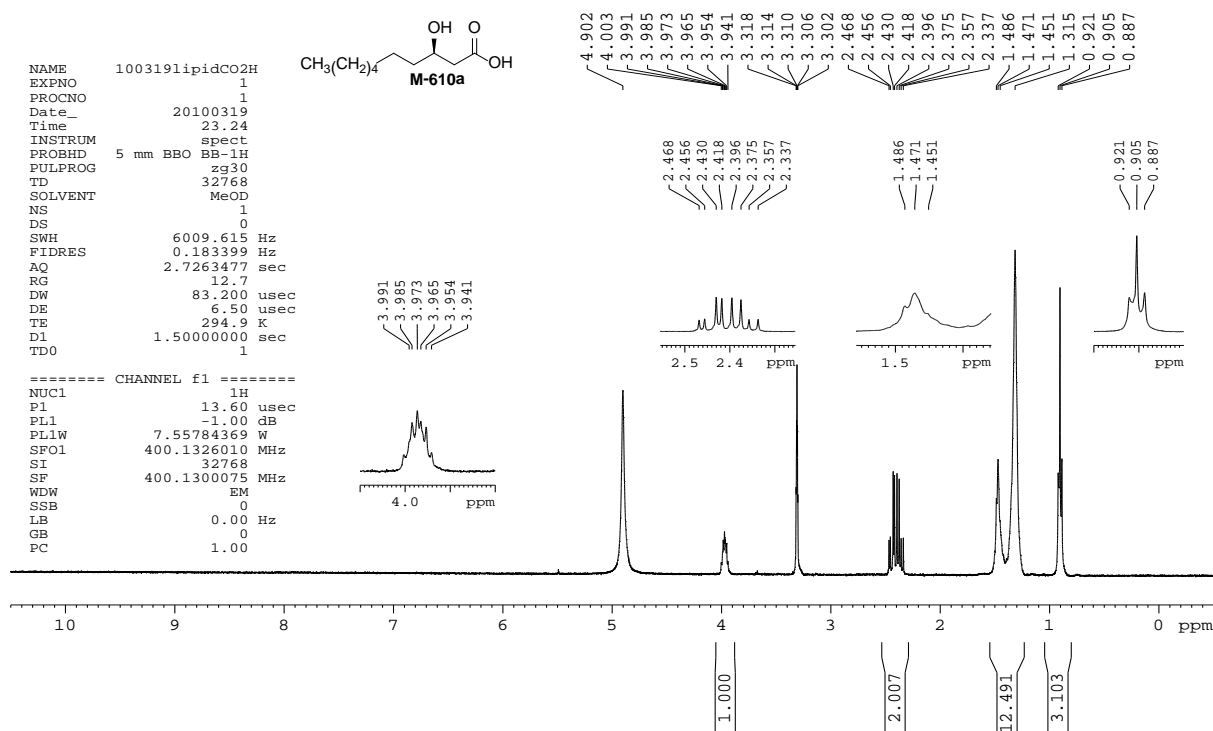
¹H NMR Spectrum of Compound M-510a



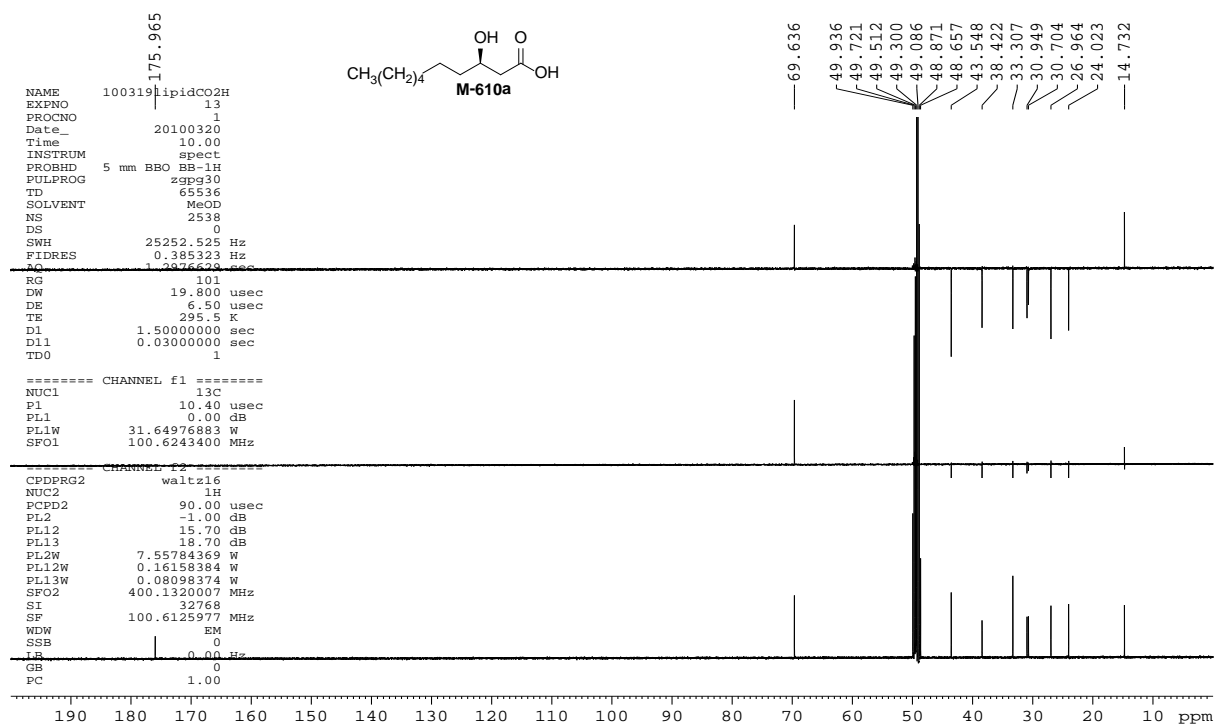
¹³C and DEPT NMR Spectrum of Compound M-510a



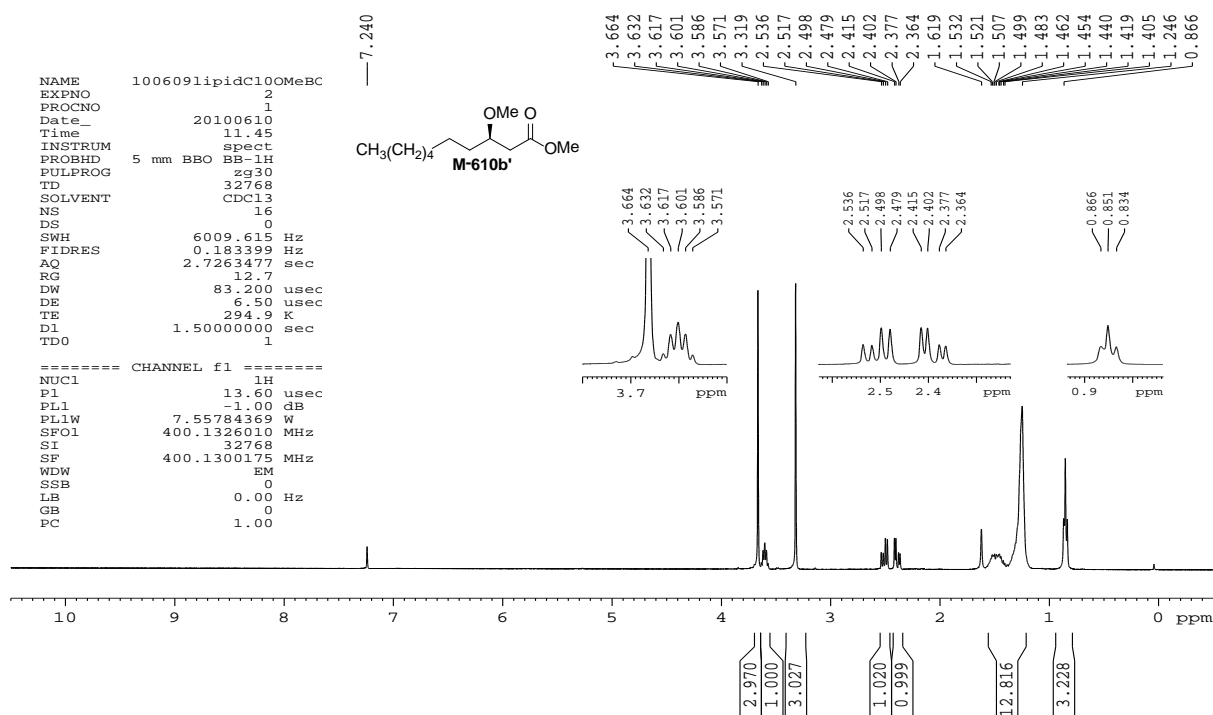
¹H NMR Spectrum of Compound M-610a



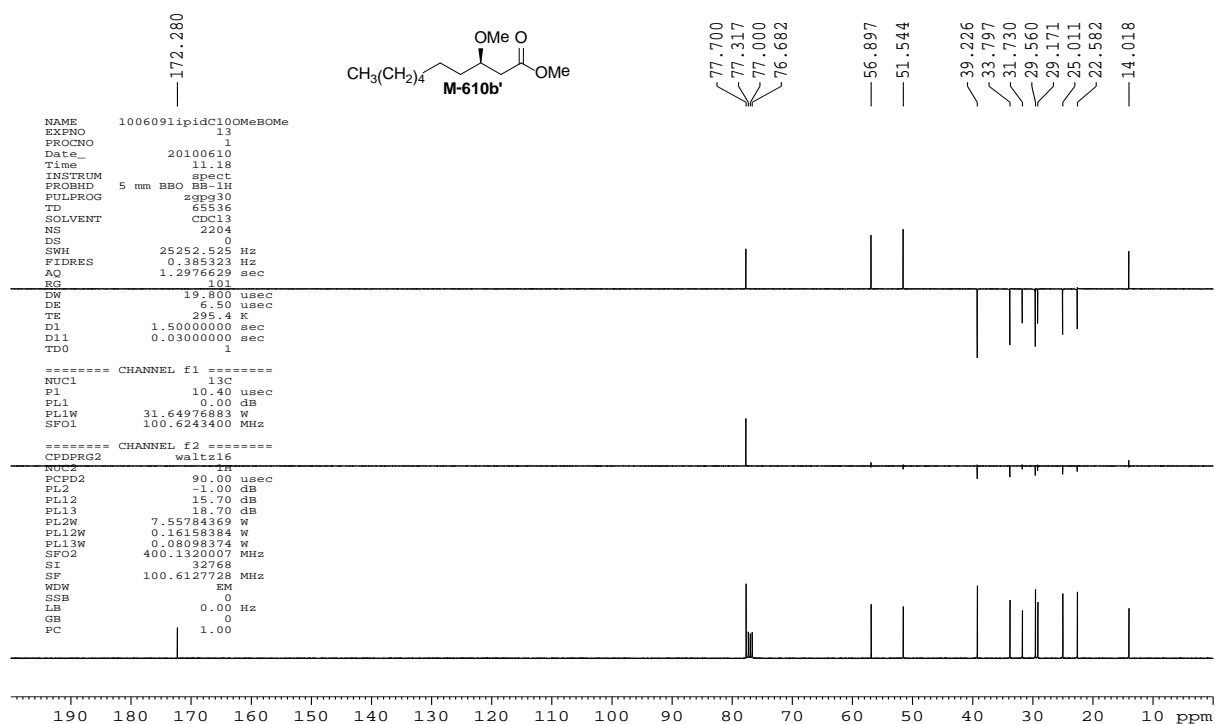
¹³C and DEPT NMR Spectrum of Compound M-610a



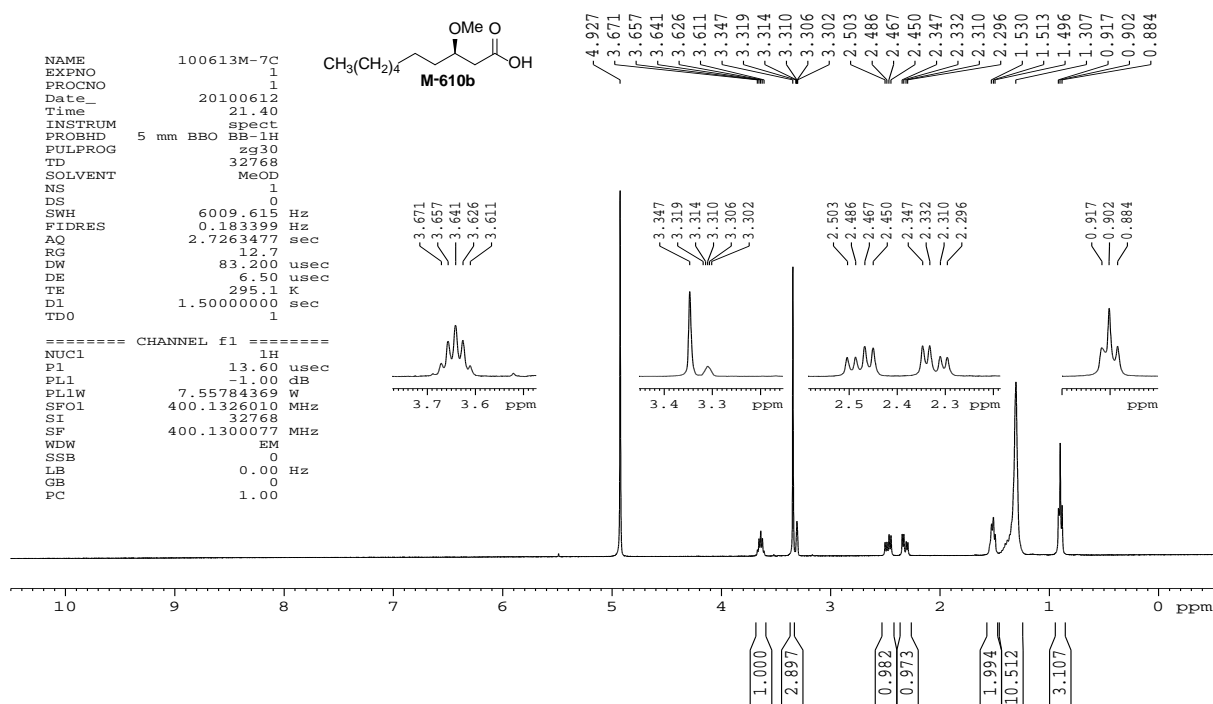
¹H NMR Spectrum of Compound M-610b'



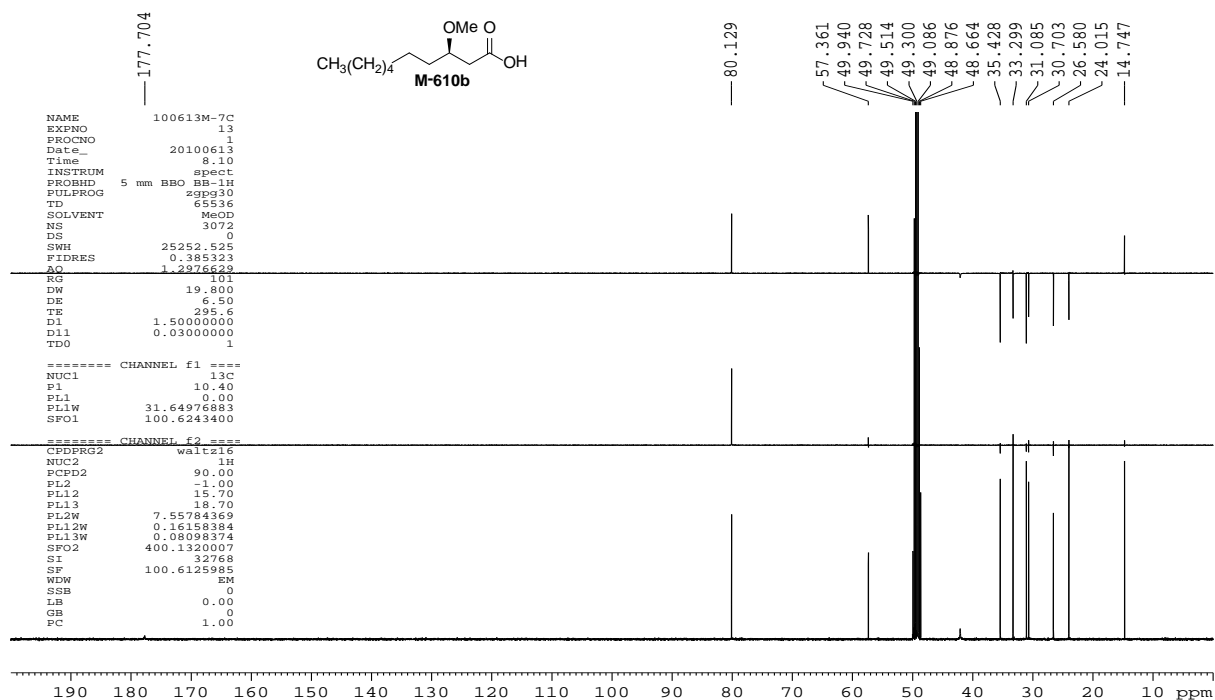
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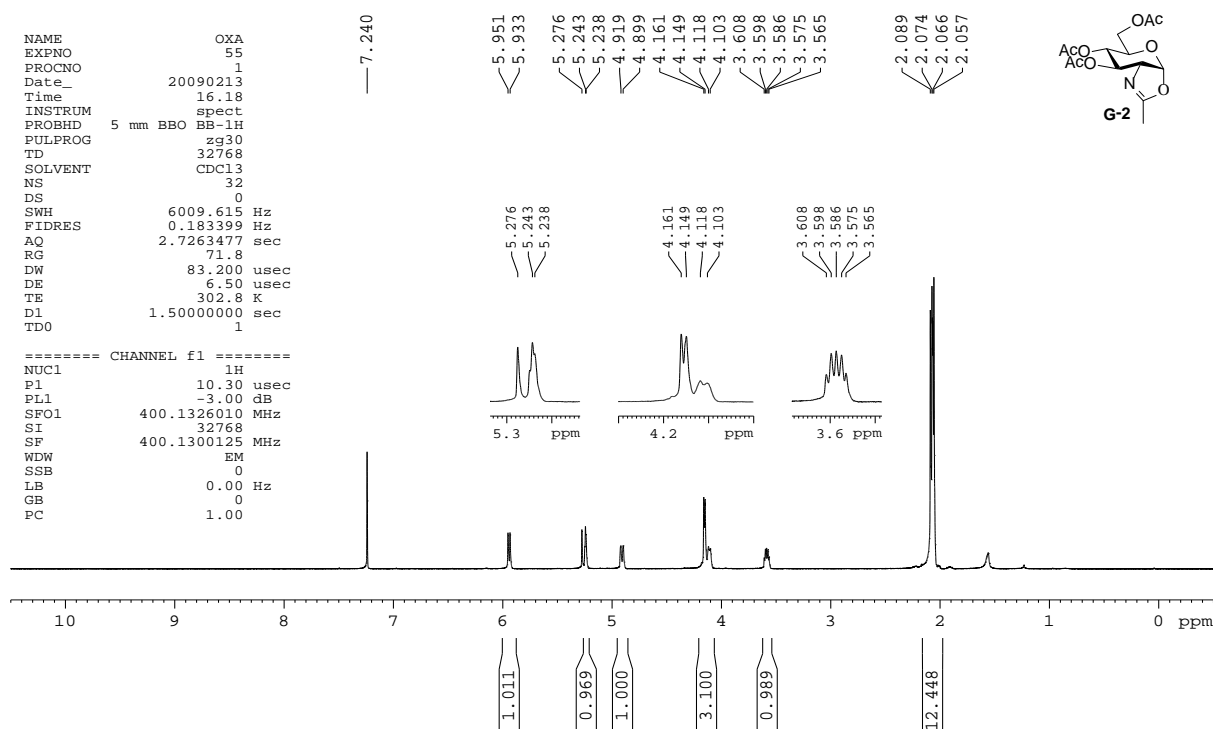
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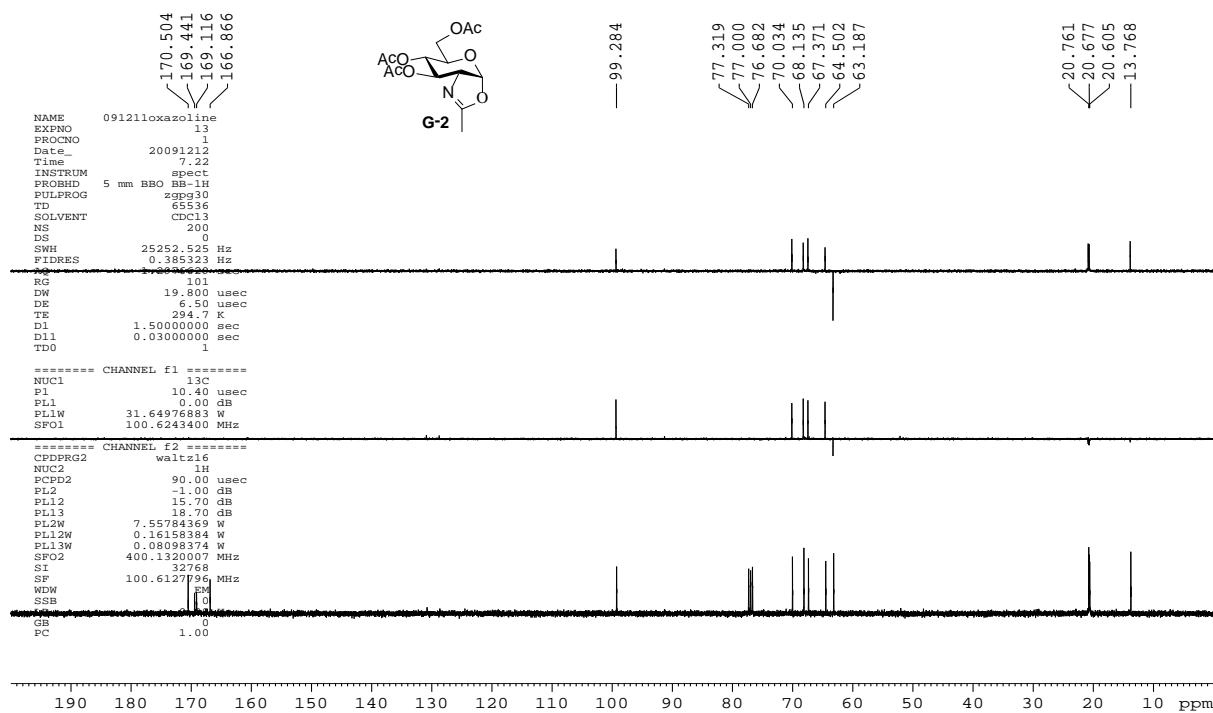
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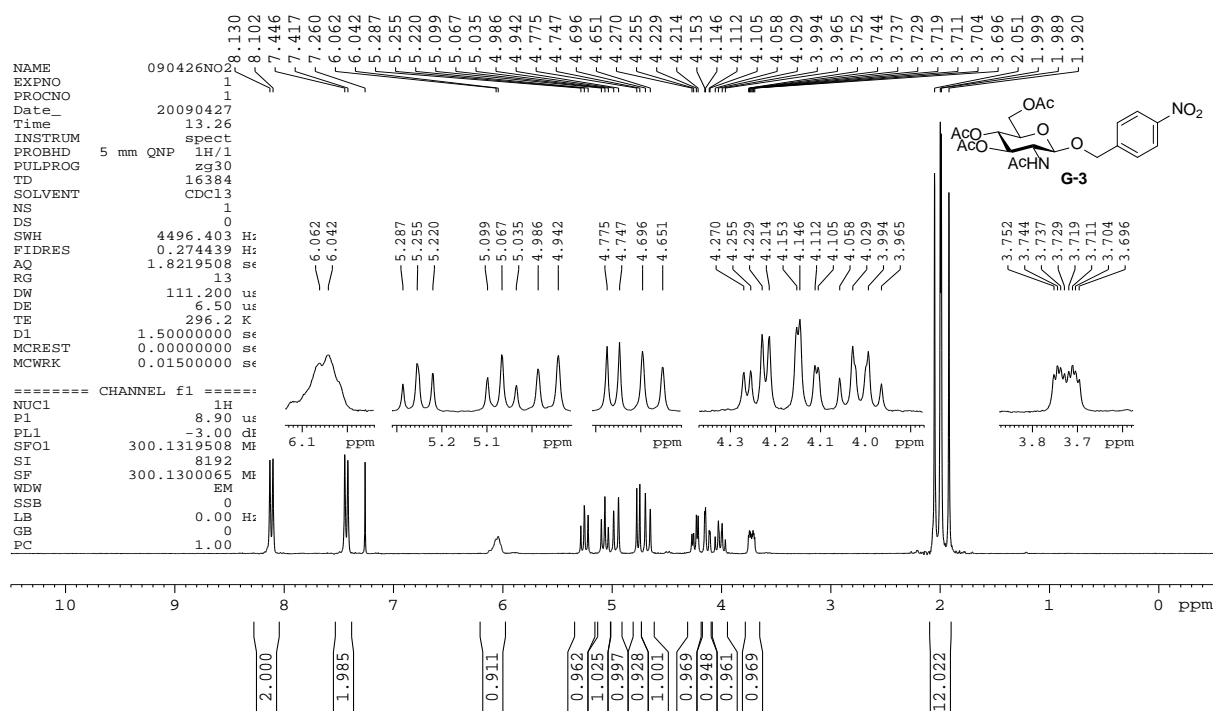
¹H NMR Spectrum of Compound G-2



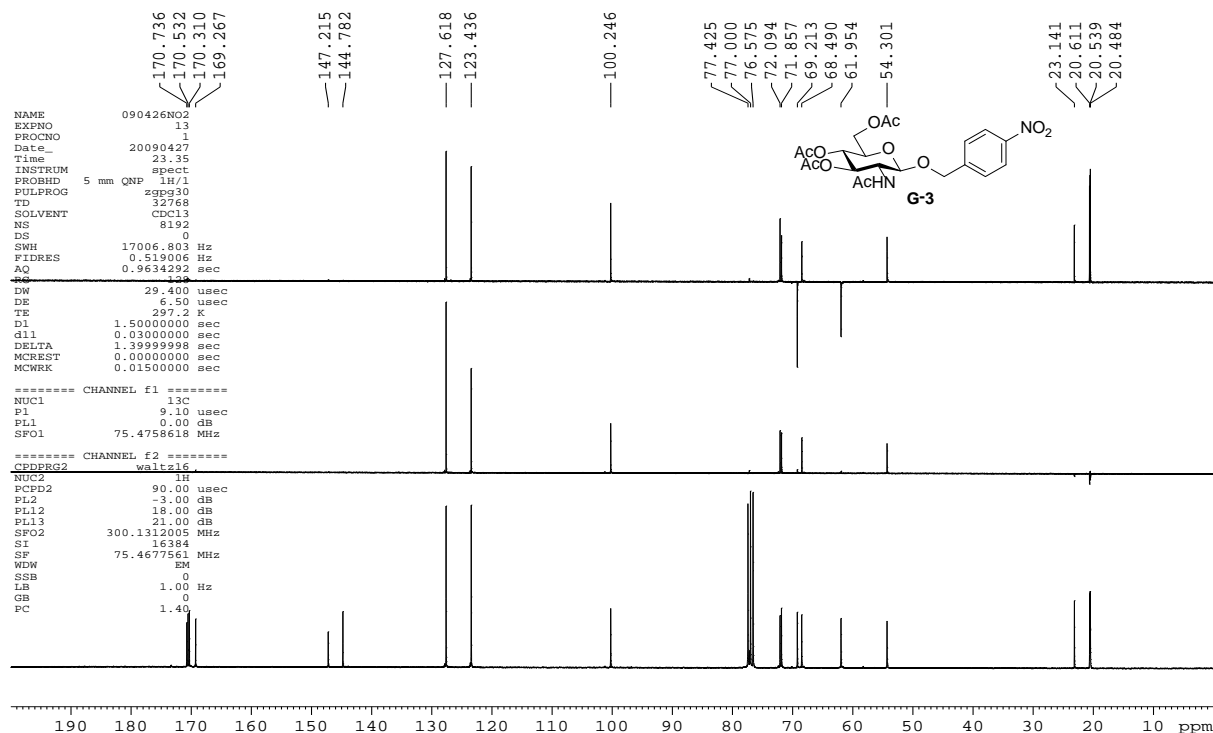
¹³C and DEPT NMR Spectrum of Compound G-2



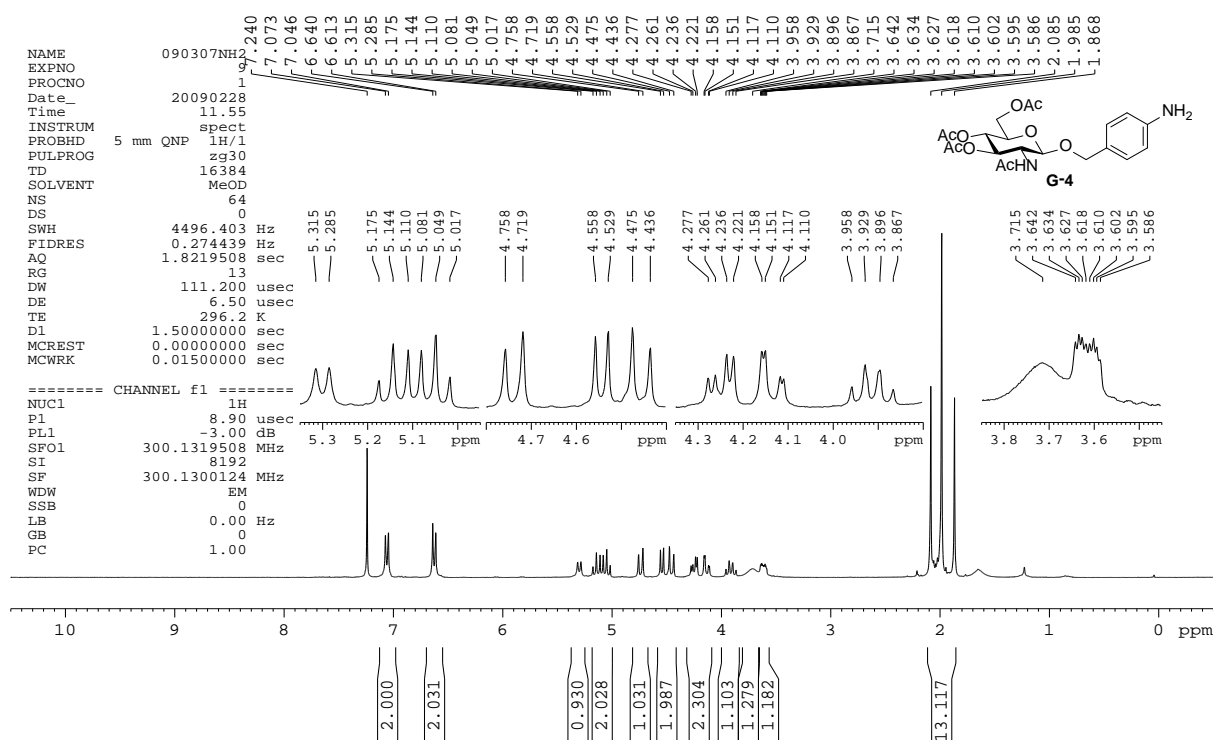
¹H NMR Spectrum of Compound G-3



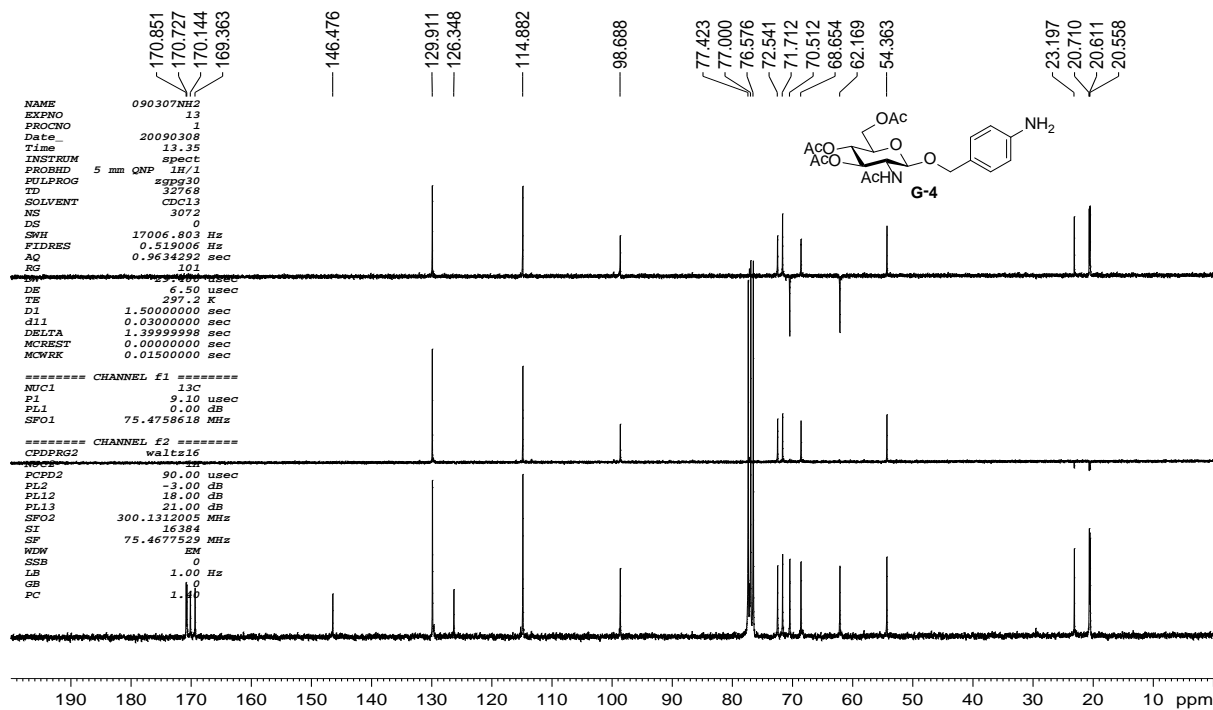
¹³C and DEPT NMR Spectrum of Compound G-3



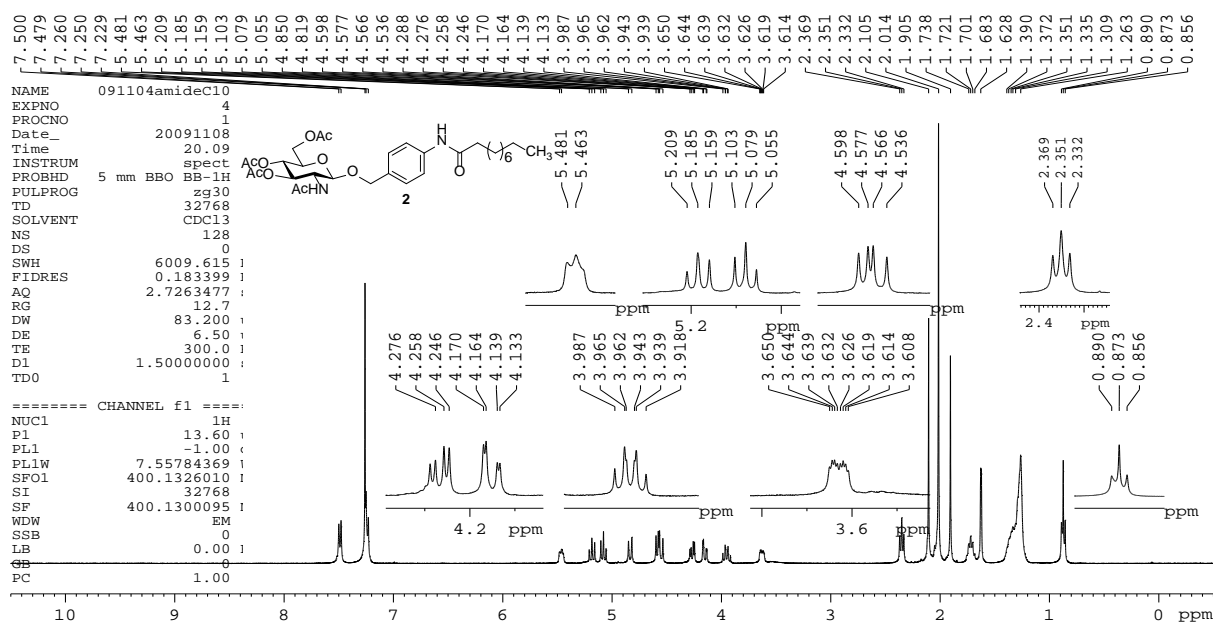
¹H NMR Spectrum of Compound G-4



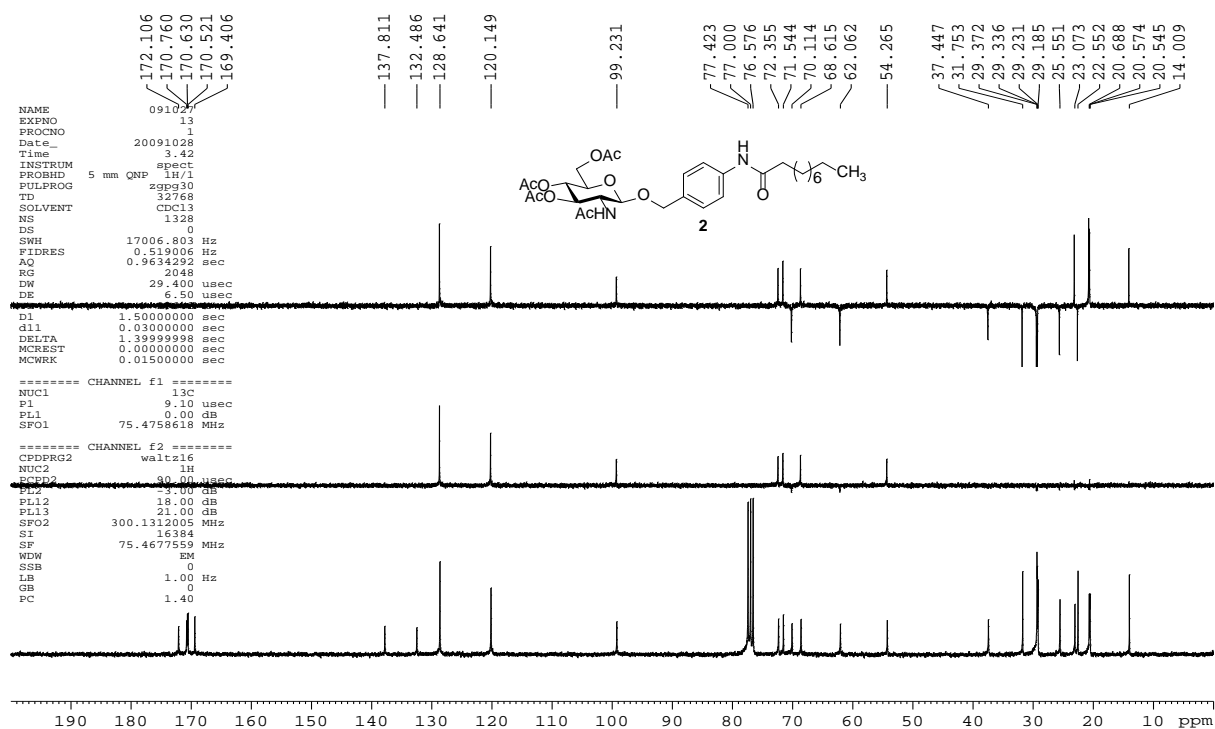
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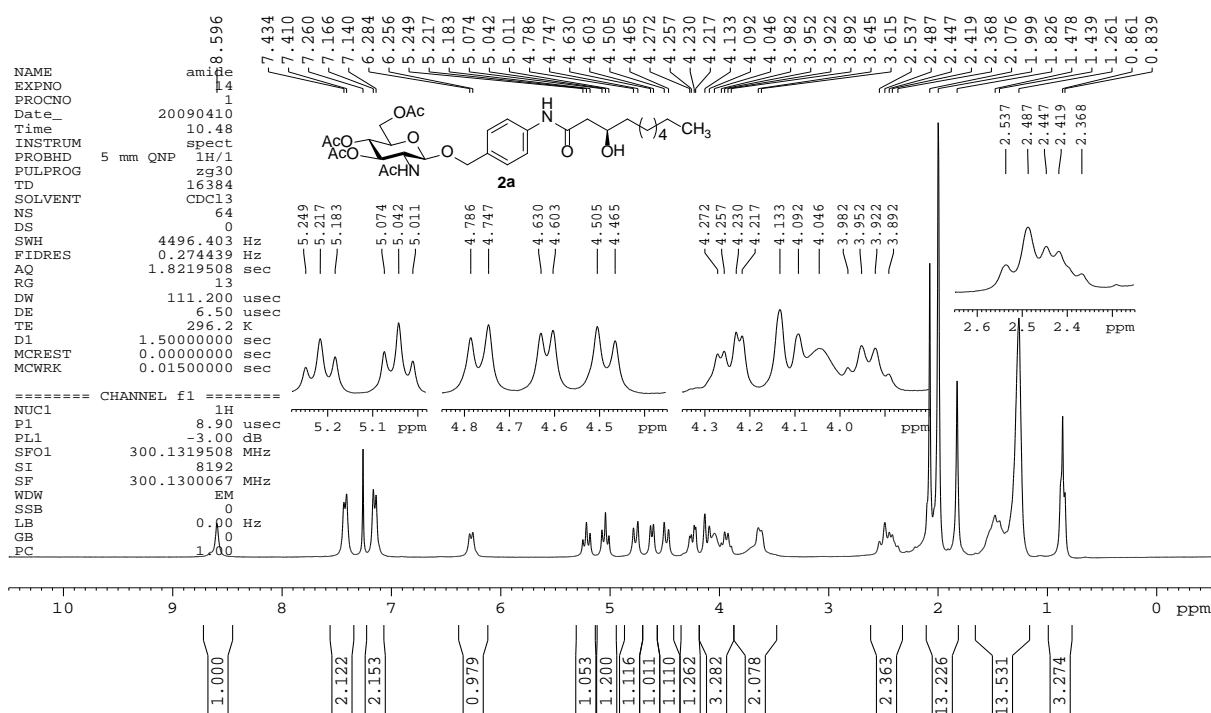
¹H NMR Spectrum of Compound 2



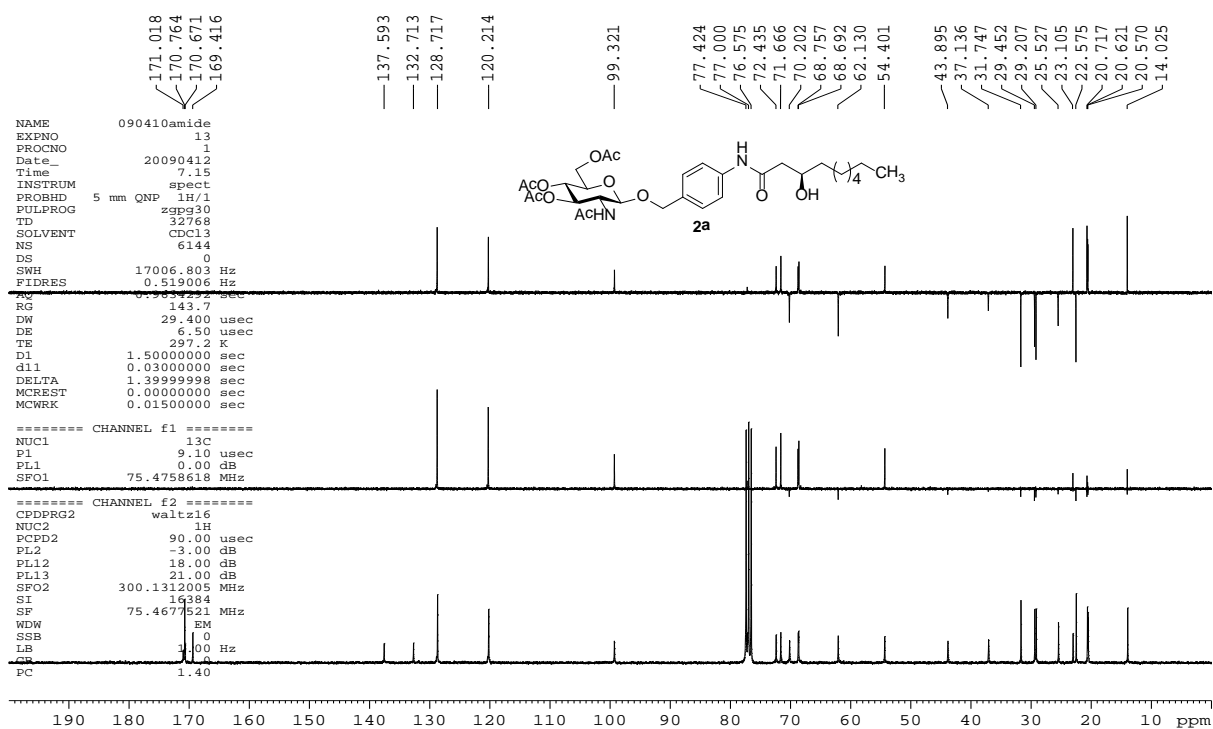
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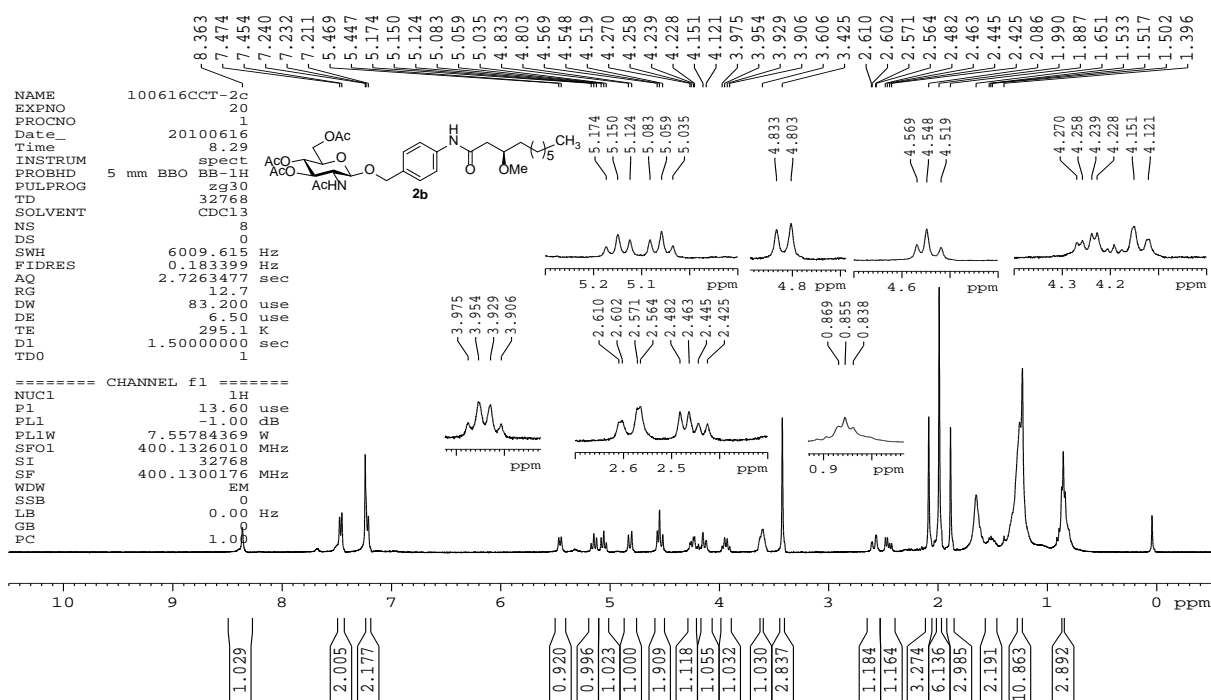
¹H NMR Spectrum of Compound 2a



¹³C and DEPT NMR Spectrum of Compound 2a



¹H NMR Spectrum of Compound 2b



¹³C and DEPT NMR Spectrum of Compound 2b

