Supporting Information for: An Aldol Condensation of an Unprotected C-Glycoside with Solid Base Catalysts

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Table of Contents

General Information. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR, respectively) spectra were acquired using Agilent DD2 400 MHz. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (J) are reported in Hz. Liquid chromatography coupled with mass spectrometry (LC-MS) analysis were recorded on a Varian 500-MS using electrospray ionization (ESI) and an Atlantis T3 column (3 μm, 2.1x150 mm). Chemicals and solvents were purchased from Fisher Chemicals, Sigma-Aldrich, Alfa-Aesar, JT Baker or TCI and used as received unless otherwise noted. All reactions were performed under ambient atmosphere unless otherwise noted. X-Ray Powder Diffraction (XRPD) measurements were performed on a Bruker D8-focus X-Ray diffractometer equipped with a Cu line-focus sealed tube, a divergent beam geometer and a NaI scintillation detector. Measurements were made with a 40 kV, 40 mA beam in the range 2θ from 3° to 80° locked couple scan type, a step size of 0.05° and a scan speed of 1 second/step. Analytical thin layer chromatography was performed on pre-coated 250 μm layer thickness silica gel 60 F254 Plates (EMD Chemicals Inc.). Visualization was performed by ultraviolet light and/or by staining with acidic ceric ammonium nitrate solution (CAM). Purifications by column chromatography or by plugs were performed using SilicaFlash F60 silica gel (40-63 μm, 230-400 mesh, Silicycle). Procedures in the following experimental are the optimized procedures. Room temperature (RT) was 20 °C ± 2 °C.

Synthesis of Hydrotalcite (HT). A solution of $Al(NO_3)_3 \cdot 9H_2O$ (18.8 g, 0.05 mol, 1 equiv.) and $Mg(NO_3)_2 \cdot 6H_2O$ (38.46 g, 0.15 mol, 3 equiv.) in distilled water (300 mL) was added dropwise over 4 h to a stirring solution of $Na_2CO_3 \cdot H_2O$ (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at *ca.* pH 10 by adding aliquots of 1 M NaOH aqueous solution. After the addition, the mixture was allowed to stir vigorously at 40 °C for three days. A white precipitate had formed and was collected by vacuum filtration and washed with distilled water (1.5 L). The filter cake was then suspended in a solution of Na_2CO_3 solution (62 g, 0.5 mol, 10 equiv.) prepared with distilled water (250 mL, 2M) and allowed to stir at 40 °C overnight. Upon completion, the precipitate was collected by vacuum filtration and washed with distilled water (2.5 L). The filter was left to dry overnight in an oven (set to 105 °C) to obtain the hydrotalcite (HT). The HT was analyzed by XRPD (Figure S1).

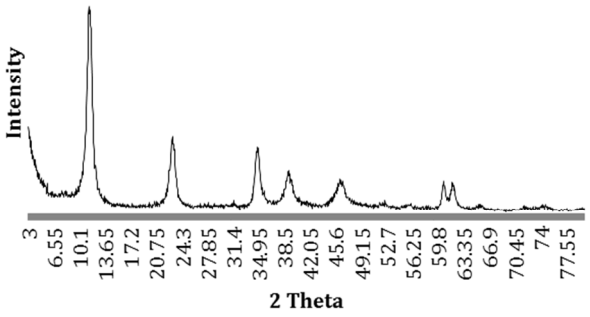


Figure S1. XRPD of HT.

Synthesis of Porous Metal Oxide (PMO). A solution of Al(NO3)3·9H2O (18.8 g, 0.05 mol, 1 equiv.) and Mg(NO3)2·6H2O (38.46 g, 0.15 mol, 3 equiv.) in distilled water (300 mL) was added dropwise over 4 h to a stirring solution of Na2CO3·H2O (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at ca. pH 10 by adding aliquots of 1 M NaOH aqueous solution. After the addition, the mixture was allowed to stir vigorously at 40 °C for three

days. A white precipitate had formed and was collected by vacuum filtration and washed with distilled water (1.5 L). The filter cake was then suspended in a solution of Na2CO3 solution (62 g, 0.5 mol, 10 equiv.) prepared with distilled water (250 mL, 2M) and allowed to stir at 40 °C overnight. Upon completion, the precipitate was collected by vacuum filtration and washed with distilled water (2.5 L). The filter was left to dry overnight in an oven (set to 105 °C) to obtain the hydrotalcite (HT). The HT solid was ground by mortar and pestle and subjected to calcination at 460 °C in air for 24 h to obtain the porous metal oxide (PMO) (8.56 g) as a white powder. The PMO was analyzed by XRPD (Figure S2).

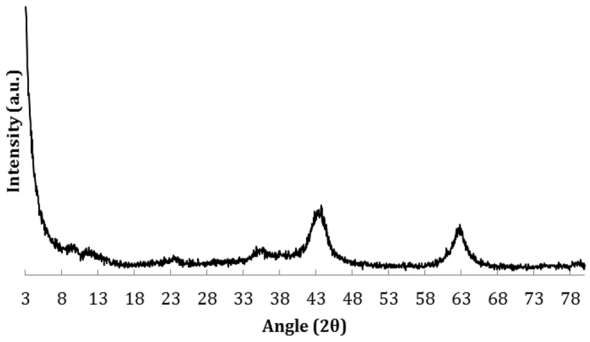


Figure S2. XRPD of PMO.

General optimized procedure for the synthesis of 2a-n. The SBC and L-proline was employed with 10-18 wt % and 1-1.5 equivalents, respectively, because of variability in the weight of the nonulose as a consequence of its high hygroscopicity. An internal standard, biphenyl (0.05 equivalent), was utilized to quantify by NMR the exact amount of nonulose that was added to each reaction which allowed the calculation of reaction conversions and product yields.

Nonulose, **1** (0.5 g, 2.27 mmol), L-proline (0.2614 g, 2.27 mmol, 1 equiv., if used), a solid base catalyst (0.05 g, 10 wt %, (either MgO or HT) and an internal standard, biphenyl (17.5 mg, 0.113 mmol, 0.05 equiv.) were added to a 4 dram vial equipped with a Teflon© coated magnetic stir bar. Methanol (5 mL) was added and the resulting solution was stirred rapidly until dissolution. Once dissolved, a small aliquot was taken for quantitative ^{1}H NMR analysis and then the aldehyde (2.71 mmol, 1.2 equiv.) was added to the reaction mixture. Then the reaction was heated to 50 °C and monitored by TLC or by LC-RI until completion. The reaction mixture was then filtered, rinsed with methanol, the filtrate collected and concentrated by rotary evaporation. The crude reaction mixture was analyzed by ^{1}H NMR to determine the conversion of **1**. The resulting crude was purified by a silica gel plug through washing with 100 % DCM, followed by 9:1 DCM:MeOH to elute the product.

If the product had precipitated during the course of the reaction, then the product was collected along with the SBC on a filter. The isolated solids were then treated with either dimethylformamide (DMF) or water (H_2O) in order to dissolve the product, and the SBC was removed by filtration. The filtrate was concentrated by rotatory evaporation to provide the desired product.

(*E*)-4-(4-methoxyphenyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetra-hydro-*2H*-pyran-2-yl)but-3-en-2-one (2a). Compound **2a** was obtained in 83 % and quantitative yields; white to light yellowish white crystalline powder; R_f = 0.42 (1.5:8.5 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.64 (d, *J* = 16 Hz, 1H), 7.61 (d, *J* = 9 Hz, 2H), 6.97 (d, *J* = 9 Hz, 2 H), 6.79 (d, *J* = 16 Hz, 1H), 3.84 (s, 3H), 3.82-3.72 (m, 2H), 3.62 (dd, *J* = 12, 5.2 Hz, 1H), 3.30-3.29 (m, 2H), 3.25-3.21 (m, 1H), 3.15 (t, *J* = 9.2 Hz, 1H), 3.1 (dd, *J* = 15.7, 2.6 Hz, 1H), 2.87 (dd, *J* = 15.7, 8.9

Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.16, 163.44, 145.02, 131.40, 128.51, 125.13, 115.49, 81.63, 79.75, 77.59, 75.18, 71.70, 62.783, 55.90, 44.25. The spectral data was consistent with the literature data.[18]

(E)-4-(4-hydroxyphenyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2b). Compound **2b** was obtained in 90 % and 58 % yields; white crystalline powder; purified by dissolving precipitate in DMF, filtration, followed by rotatory evaporation; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.01 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.5 (d, *J* = 16.2 Hz, 1H), 6.8 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 16.2 Hz, 1H), 5.01 (d, *J* = 5.7 Hz, 1H), 4.90 (d, *J* = 4.7 Hz, 1H), 4.83 (d, *J* = 4.7 Hz, 1H), 4.32 (t, *J* = 5.7 Hz, 1H) 3.62-3.56 (m, 2H), 3.41-3.35 (m 1H), 3.19-3.13 (m, 1H), 3.10-3.04 (m, 2H), 2.97-2.88 (m, 2H), 2.74 (dd, *J* = 15.8, 9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.71, 159.81, 142.40, 130.42, 125.44, 123.58, 115.79, 80.67, 78.13, 75.87, 73.56, 70.29, 61.11, 43.17. *m/z* (LC-MS) 325.2, Calcd $[M+H]^+$ 325.128.

(E)-4-phenyl-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2c). Compound **2c** obtained in 91 & 92 % yields; beige-white powder; R_f = 0.18 (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.64 (d, *J* = 16.2 Hz, 1H), 7.62 (m, 2H), 7.39 (t, *J* = 3.1 Hz, 3H), 6.90 (d, *J* = 16.2 Hz, 1H), 3.77-3.72 (m, 2H), 3.60 (dd, *J* = 11.9, 5.1 Hz, 1H), 3.37-3.31 (m, 2H), 3.24-3.19 (m, 1H), 3.16-3.08 (m, 2H), 2.89 (dd, *J* = 15.8, 9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.01, 144.84, 136.02, 131.69, 130.04, 129.55, 127.49, 81.64, 79.74, 77.49, 75.15, 71.70, 62.77, 44.38. *m/z* (LC-MS) 309.3, Calcd $[M+H]^+$ 309.133.

(E)-4-(furan-2-yl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2d). Compound **2d** obtained in 87 % & Quantitative yields; yellow crystalline solid; R_f = 0.13 (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.66 (d, *J* = 1.6 Hz, 1H), 7.45 (d, *J* = 15.8 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.69 (d, *J* = 15.8 Hz, 1H), 6.57 (dd, *J* = 3.4, 1.9 Hz,

1H), 3.75 (m, 2H), 3.62 (dd, *J* = 11.9, 5.1 Hz, 1H), 3.35 (m, 2H), 3.24-3.21 (m, 1H), 3.14 (t, *J* = 9.1 Hz, 1H), 3.07 (dd, *J* = 15.8, 2.7 Hz, 1H), 2.85 (dd, *J* = 15.7, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 200.63, 152.46, 146.86, 131.09, 124.61, 117.52, 113.76, 81.63, 79.73, 77.54, 75.14, 71.68, 62.75, 44.32. matched literature.[18]

(E)-4-(4-hydroxy-3-methoxyphenyl)-1-(3,4,5-trihydroxy-6-(hydroxylmethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2e). Compound **2e** obtained in 98 & 88 % yields; whitish yellow powder; R_f = 0.24 (1.5:8.5 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.61 (d, *J* = 16 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.14 (dd, *J* = 8.2, 1.8 Hz, 1H) 6.82 (d, *J* = 8.2, 1H), 6.77 (d, *J* = 16 Hz, 1H), 3.90 (s, 3H), 3.79-3.71 (m, 2H), 3.63 (dd, *J* = 11.9, 5.1 Hz, 2H), 3.39-3.34 (m, 2H), 3.26-3.21 (m, 1H), 3.15 (t, H = 9.1 Hz, 1H), 3.10 (dd, *J* = 15.7, 2.5 Hz, 1H), 2.87 (dd, *J* = 15.7, 8.9, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.21, 150.99, 149.43, 145.84, 127.86, 124.72, 124.54, 116.56, 111.97, 81.63, 79.74, 77.63, 75.20, 71.70, 62.78, 56.47, 44.25. *m/z* (LC-MS) 355.3, Calcd $[M+H]^+$ 355.139.

(E)-4-(benzo[d][1,3]dioxol-5-yl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)-tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2f). Compound **2f** obtained in 87 & 90 % yields; beige white powder; R_f = 0.18 (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.56 (d, *J* = 16.2 Hz, 1H), 7.18 (s, 1H), 7.11 (d, *J* = 8 Hz, 1H), 6.84 (d, *J* = 8 Hz, 1H), 6.74 (d, *J* = 16Hz, 1H), 5.99 (s, 2H), 3.78-3.72 (m, 2H), 3.62 (dd, *J* = 11.8, 5 Hz, 1H), 3.39-3.24 (m, 2H), 3.25-3.21 (m, 1H), 3.15 (t, *J* = 9.2 Hz, 1H) 3.09 (dd, *J* = 15.8, 2.5 Hz, 1H), 2.86 (dd, *J* = 15.8, 9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.04, 151.54, 149.96, 144.93, 130.37, 126.45, 125.51, 109.51, 107.61, 103.11, 81.60, 79.72, 77.54, 75.15, 71.68, 62.75, 44.35. matched literature.[18]

4-((E)-3-oxo-4-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-1-en-1-yl)benzoic acid (2g). Compound **2g** obtained in 26 & 20 % yields; beige powder; purified by

dissolving in basic H_2O, filtered from SBC and then re-precipitated with acidic H_2O; ^{1}H NMR (400 MHz, CD_3OD): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 16.2, 1H), 7.7 (d, *J* = 8.2, 2H), 6.97 (d, *J* = 16.2 Hz, 1H), 3.83-3.77 (m, 2 H), 3.65 (dd, *J* = 12.2, 5 Hz, 1H), 3.47-3.33 (m, 3 H), 3.24 (t, *J* = 9.2 Hz, 1H), 3.19 (dd, *J* = 15.9, 2.8 Hz, 1H), 2.96 (dd, *J* = 16, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.10, 166.85, 140.61, 136.67, 132.07, 129.73, 128.74, 128.49, 80.73, 78.12, 75.80, 73.60, 70.31, 61.14, 43.64. *m/z* (LC-MS) 353.3, Calcd $[M+H]^+$ 353.123.

methyl 4-((E)-3-oxo-4-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-1-en-1-yl)benzoate (2h). Compound **2h** obtained in 86 & 72 % yields; light yellowish white powder; R_f = 0.31 (1:9 MeOH:DCM);); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 16.4 Hz, 1H), 7.07 (d, *J* = 16.2 Hz, 1H), 5.05 (d, *J* = 5.9 Hz, 1H), 4.92 (d, *J* = 4.7 Hz, 1H), 4.85 (d, *J* = 4.1 Hz, 1H), 4.35 (t, D = 5.7 Hz, 1H), 3.87 (s, 3H), 3.65-3.57 (m, 2H), 3.41-3.36 (m, 1H), 3.20-3.14 (m, 1H), 3.08-3.05 (m, 2H), 3.00-3.92 (m, 2H), 2.81 (dd, *J* = 16 Hz, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.08, 165.74, 140.36, 139.15, 130.63, 129.58, 129.02, 128.63, 80.73, 78.10, 75.78, 73.60, 70.30, 61.13, 52.28, 43.66. *m/z* (LC-MS) 367.3, Calcd $[M+H]^+$ 367.139.

(E)-4-(4-(trifluoromethyl)phenyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)-tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2i). Compound **2i** obtained in 97 % & quantitative yields; white powder; R_f =0.15 (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, DMSO-d6 & CD3OD): δ 7.88 (d, *J* = 8 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 16.2 Hz, 1H), 7.03 (d, *J* = 16.2 Hz, 1H), 3.68-3.59 (m, 2H), 3.44-3.40 (m, 1H), 3.22-3.17 (m, 1H), 3.10-3.09 (m, 2H), 3.01-2.96 (m, 2H), 2.81 (dd, *J* = 16, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d6 & CD3OD): δ 198.62, 140.61, 139.16, 130.73 (q, *J* = 32.3x3 Hz), 129.60, 129.38, 126.09 (q, *J* = 3.5x3 Hz), 124.54 (q, *J* = 271.7x3 Hz), 81.09, 78.55, 76.33, 74.04, 70.73, 61.64, 44.04. m/z (LC-MS) 377.2, Calcd [M+H]+ 377.121.

(E)-4-(4-(dimethylamino)phenyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2j). Compound **2j** obtained in 92 & 81 % yields; orangey yellow to reddish yellow powder; R_f = 0.81 (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.61 (d, *J* = 16 Hz, 1H), 7.51 (d, *J* = 9 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 15.8 Hz, 1H), 3.79-3.71 (m, 2H), 3.62 (dd, *J* = 11.9, 5.1 Hz, 1H), 3.39-3.29 (m, 2H), 3.25-3.20 (m, 1H), 3.15 (t, *J* = 9.2 Hz, 1H), 3.09 (dd, *J* = 15.5, 2.5 Hz, 1H), 3.03 (s, 6H), 2.84 (dd, *J* = 15.6, 9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.25, 153.95, 146.62, 131.53, 123.29, 121.94, 113.01, 81.62, 79.76, 77.78, 75.23, 71.70, 62.79, 44.05, 40.22. matched literature.[18]

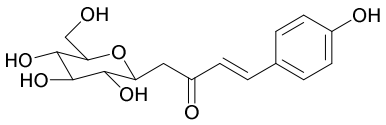
(E)-4-(3,5-dimethylphenyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2k). Compound **2k** obtained in 99 % & quantitative yields; creamy peachy white solid; R_f = 0.19 (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.59 (d, *J* = 16.2 Hz, 1H), 7.25 (s, 2H), 7.07 (s, 1H), 6.87 (d, *J* = 16.2, 1H), 3.79-3.74 (m, 2H), 3.63 (dd, *J* = 11.9, 5.1 Hz, 1H), 3.40-3.29 (m, 2H), 3.26-3.21 (m, 1H), 3.16 (t, *J* = 9 Hz, 1H), 3.12, (dd, *J* = 15.9, 2.8 Hz, 1H), 2.89, (dd, *J* = 15.7, 8.9 Hz,1H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.14, 145.36, 139.76, 135.85, 133.39, 127.37, 127.04, 81.62, 79.73, 77.49, 75.14, 71.68, 62.76, 44.33, 21.19. *m/z* (LC-MS) 337.3, Calcd $[M+H]^+$ 337.165.

(E)-4-([1,1'-biphenyl]-4-yl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2l). Compound **2l** obtained in a quantitative & 99 % yields; yellowish white powder purified by dissolving in DMF, filtrating, followed by rotatory evaporation (1:9 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H) overlapping with 7.73 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 16.2 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 16.2 Hz, 1H), 5.06 (d, *J* = 5.7 Hz, 1H), 4.93 (d, *J* = 4.5 Hz, 1H), 4.86 (d, *J* = 4.5 Hz, 1H), 4.35 (t, *J* = 5.7 Hz, 1H), 3.66-3.58 (m, 2H), 3.43-3.37 (m, 1H),

3.21-3.16 (m, 1H), 3.12-3.05 (m, 2H), 3.00-2.94 (m, 2H), 2.82 (dd, *J* = 16.0, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 198.44, 142.26, 141.93, 139.62, 134.09, 129.54, 129.44, 128.38, 127.51, 127.18, 127.10, 81.13, 78.55, 76.24, 74.01, 70.72, 61.55, 43.88. *m/z* (LC-MS) 385.3, Calcd $[M+H]^+$ 385.165.

(E)-4-(4-(tert-butyl)phenyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-*2H*-pyran-2-yl)but-3-en-2-one (2m). Compound **2m** obtained in 96 & 95 % yields; beige powder; R_f = 0.17; ^{1}H NMR (400 MHz, CD_3OD): δ 7.65 (d, *J* = 16.2 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 16 Hz, 1H), 3.79-3.74 (m, 2H), 3.63 (dd, *J* = 12, 5.2 Hz, 1H), 3.39-3.29 (m, 2H), 3.26-3.22 (m, 1H), 3.16 (t, *J* = 9 Hz, 1H), 3.12 (dd, *J* = 15.8, 2.5, 1H), 2.9 (dd, *J* = 15.8, 9 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.12, 155.50, 144.91, 133.21, 129.47, 127.01, 126.70, 81.63, 79.74, 77.52, 75.15, 71.70, 62.77, 44.29, 35.77, 31.54. *m/z* (LC-MS) 365.4, Calcd $[M+H]^+$ 365.196.

(E)-4-(p-tolyl)-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)but-3-en-2-one (2n). Compound **2n** obtained in 91 & 92 % yields; beige white powder; R_f = 0.34 (1.5:8.5 MeOH:DCM); ^{1}H NMR (400 MHz, CD_3OD): δ 7.64 (d, *J* = 16.2 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 16.2 Hz, 1H), 3.79-3.73 (m, 2H), 3.62 (dd, *J* = 11.9, 5.1 Hz, 1H), 3.39-3.29 (m, 2H), 3.25-3.21 (m, 1H), 3.18-3.09 (m, 2H), 2.89 (dd, *J* = 15.8, 8.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 201.13, 145.04, 142.46, 133.21, 130.71, 129.61, 126.50, 81.61, 79.72, 77.50, 75.14, 71.68, 62.761, 44.29, 21.49. matched literature.[18]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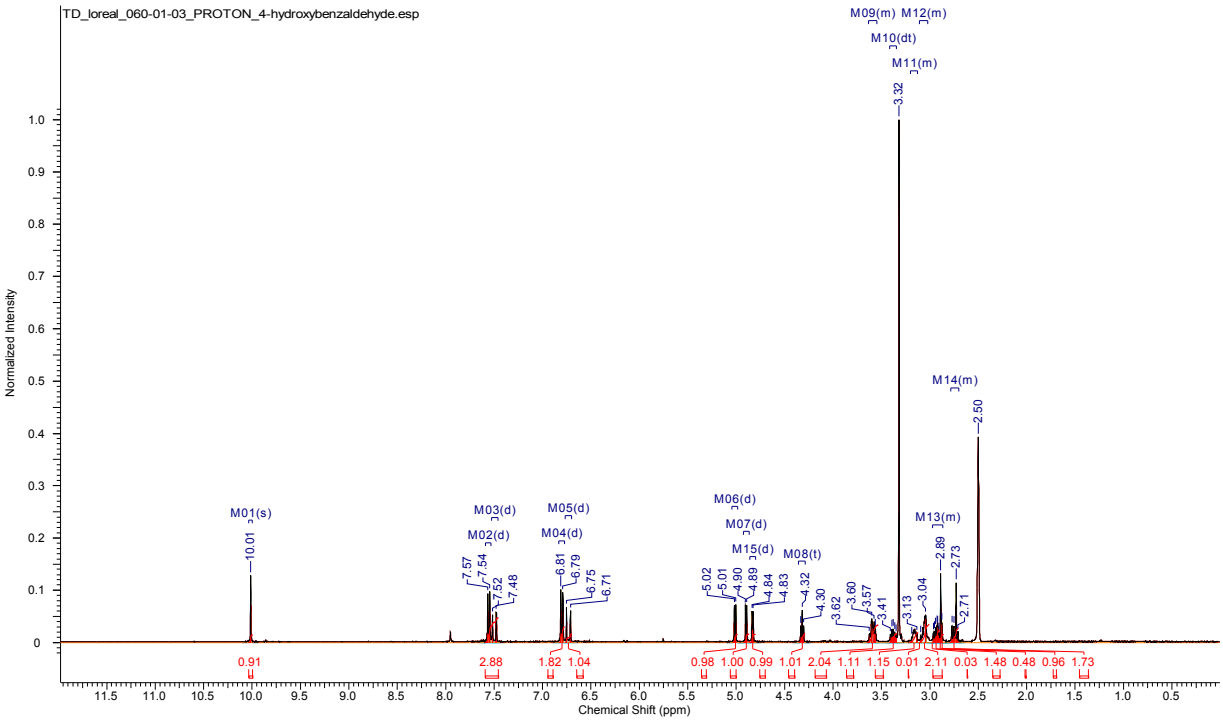
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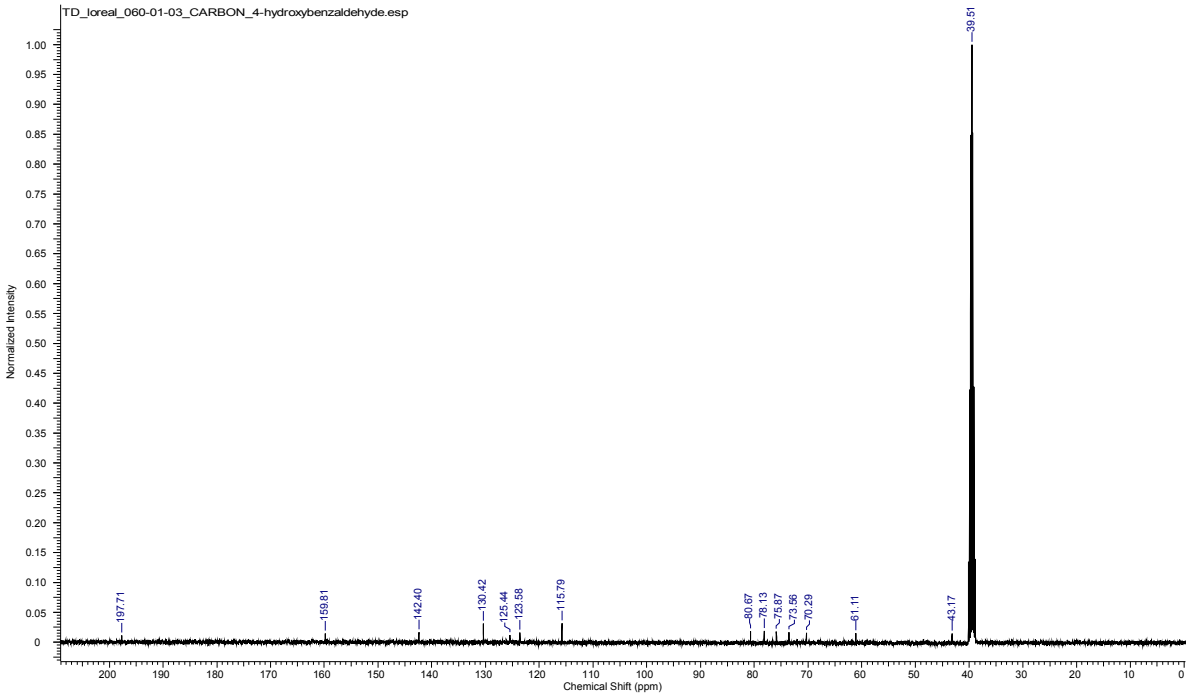
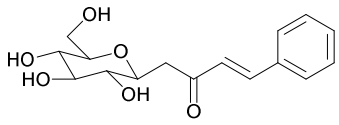
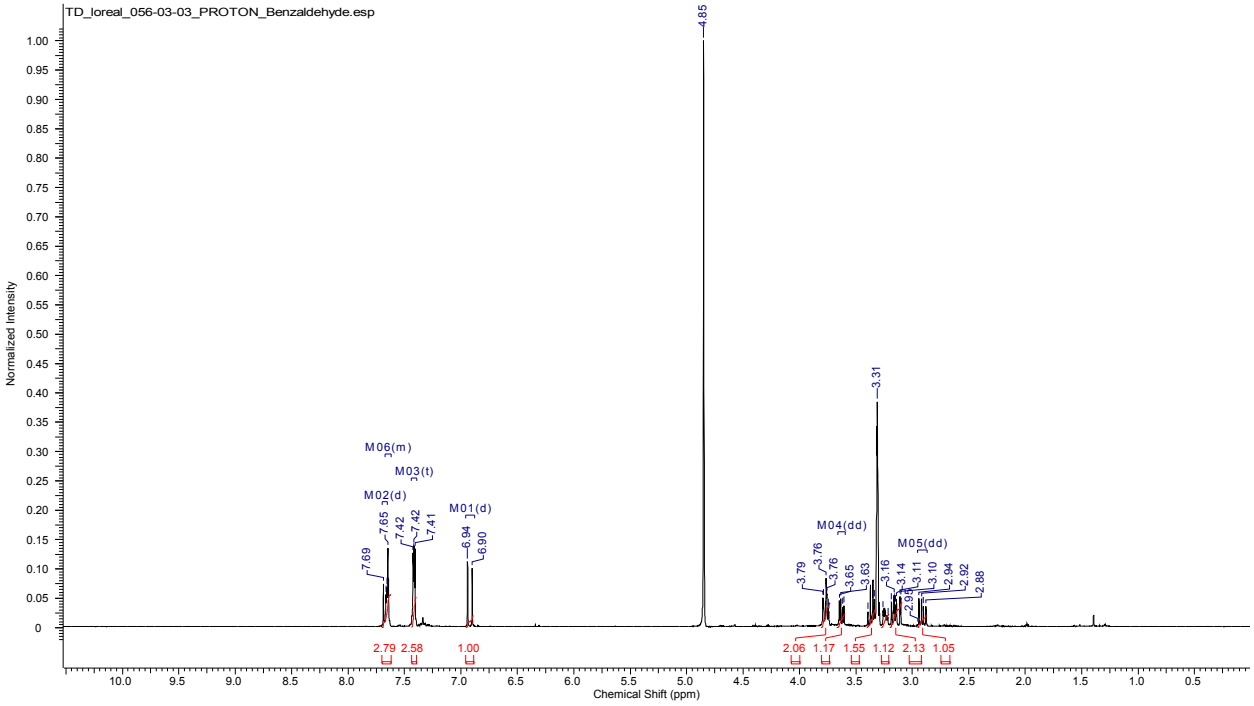
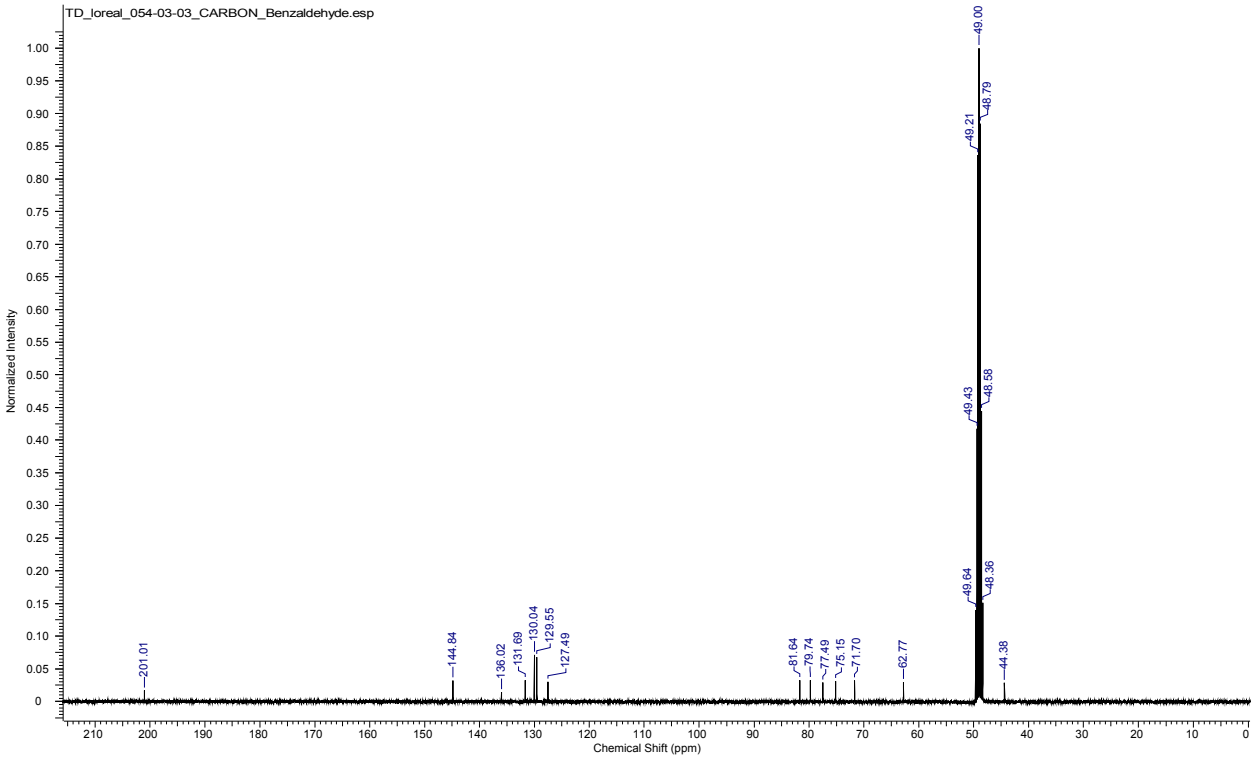
10.01
7.57
7.54
7.52
7.48
6.81
6.79
6.75
6.71
5.02
5.01
4.90
4.89
4.84
4.83
4.32
4.30
3.62
3.60
3.57
3.41
3.32
3.13
3.04
2.89
2.73
2.71
2.50
0.91
2.88
1.82
1.04
0.98
1.00
0.99
1.01
2.04
1.11
1.15
0.01
2.11
0.03
1.48
0.48
0.96
1.73
Normalized Intensity
Chemical Shift (ppm)

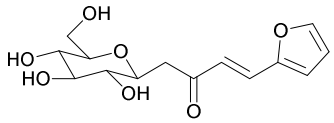

TD_loreal_060-01-03_CARBON_4-hydroxybenzaldehyde.esp
197.71
159.81
142.40
130.42
125.44
123.58
115.79
80.67
78.13
75.87
73.56
70.29
61.11
43.17
39.51
Normalized Intensity
Chemical Shift (ppm)


OH
HO
HO
O
OH
O

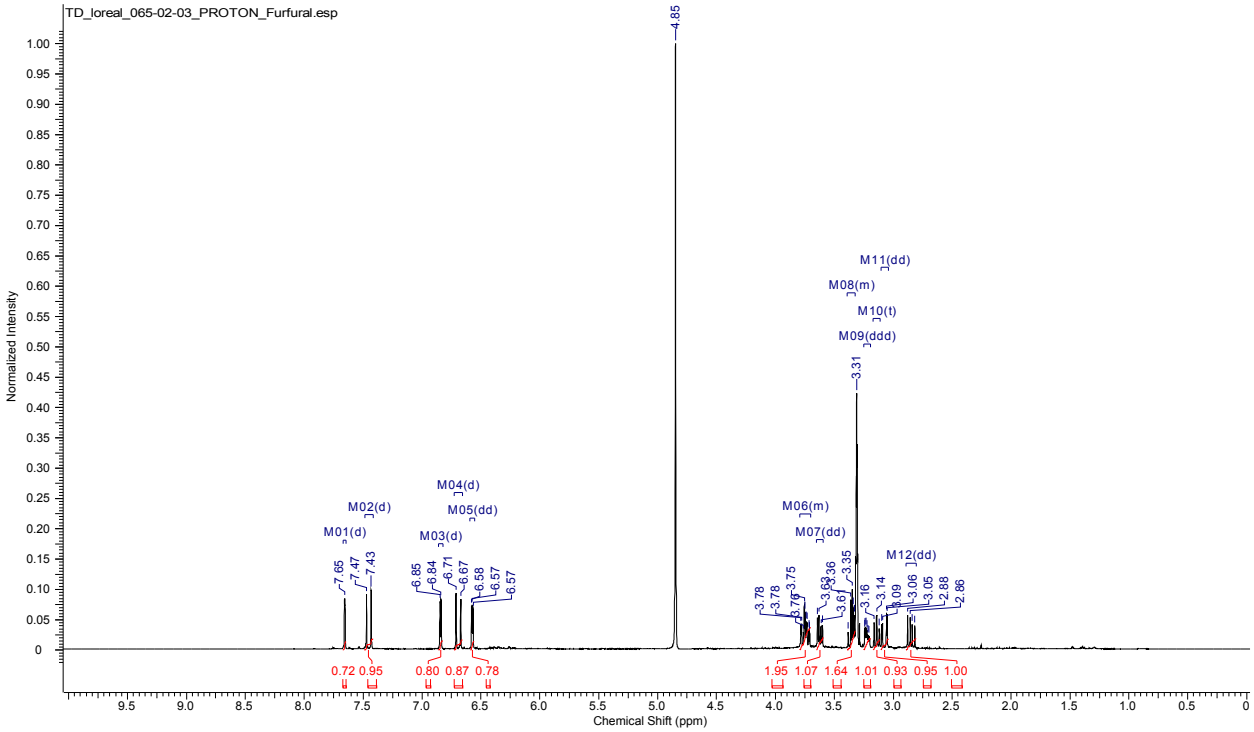
2c

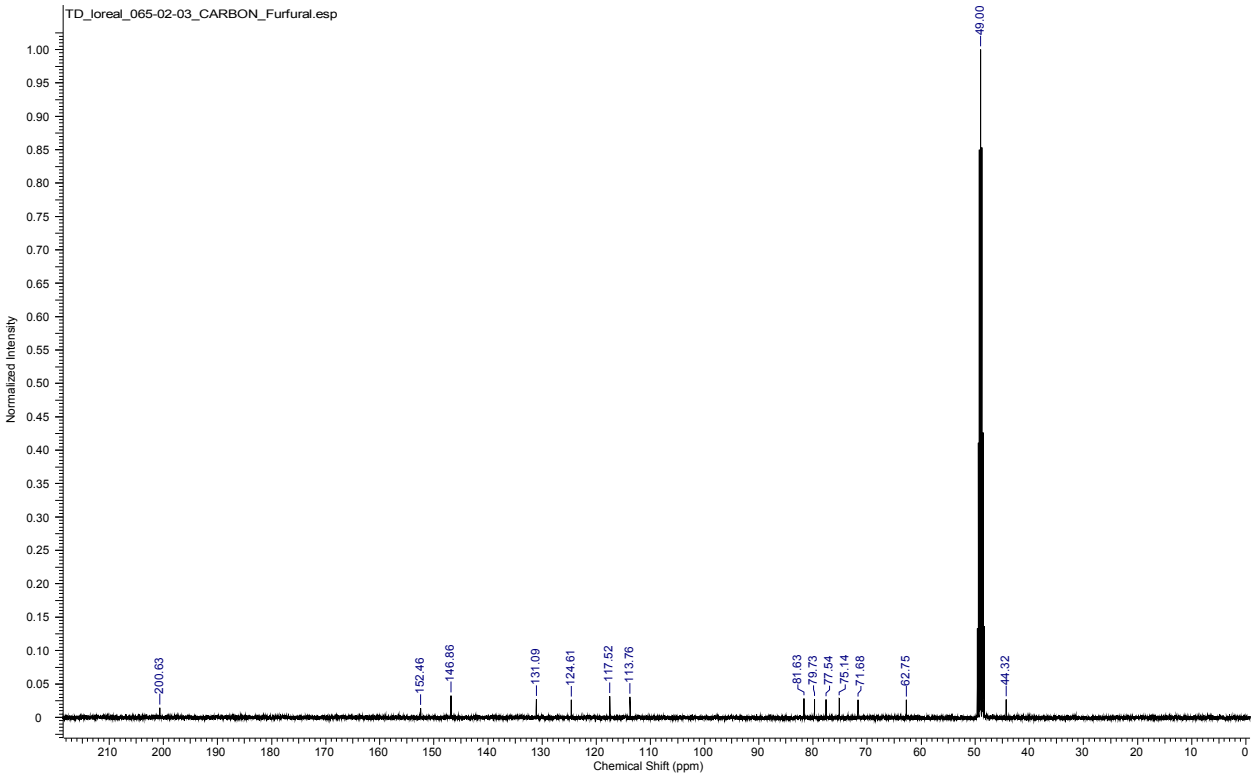

TD_loreal_056-03-03_PROTON_Benzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
4.85
3.31
M06(m)
M03(t)
M02(d)
M01(d)
M04(dd)
M05(dd)
7.69
7.65
7.42
7.42
7.41
6.94
6.90
3.79
3.76
3.76
3.65
3.63
3.16
3.14
3.11
3.10
2.94
2.92
2.88
2.79
2.58
1.00
2.06
1.17
1.55
1.12
2.13
1.05

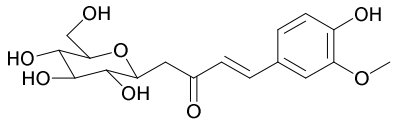

TD_loreal_054-03-03_CARBON_Benzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
49.00
48.79
49.21
49.43
48.58
49.64
48.36
201.01
144.84
136.02
131.69
130.04
129.55
127.49
81.64
79.74
77.49
75.15
71.70
62.77
44.38


OH
HO
HO
O
OH
O
O

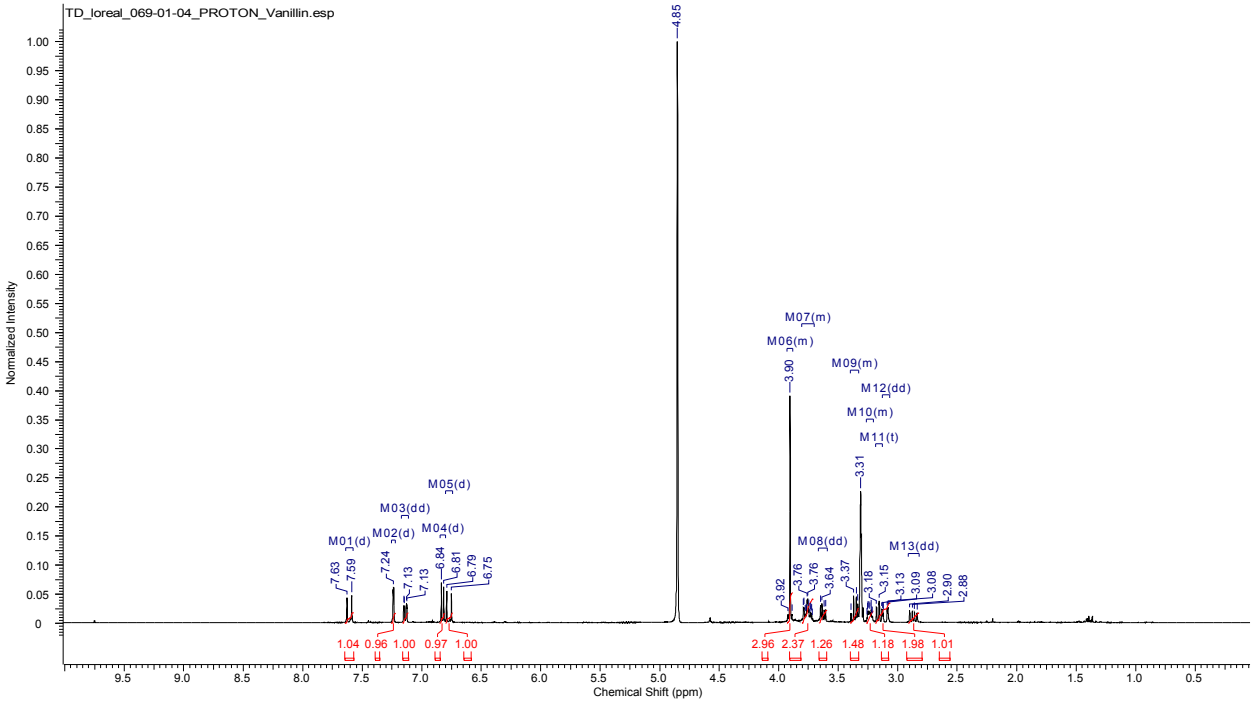
2d

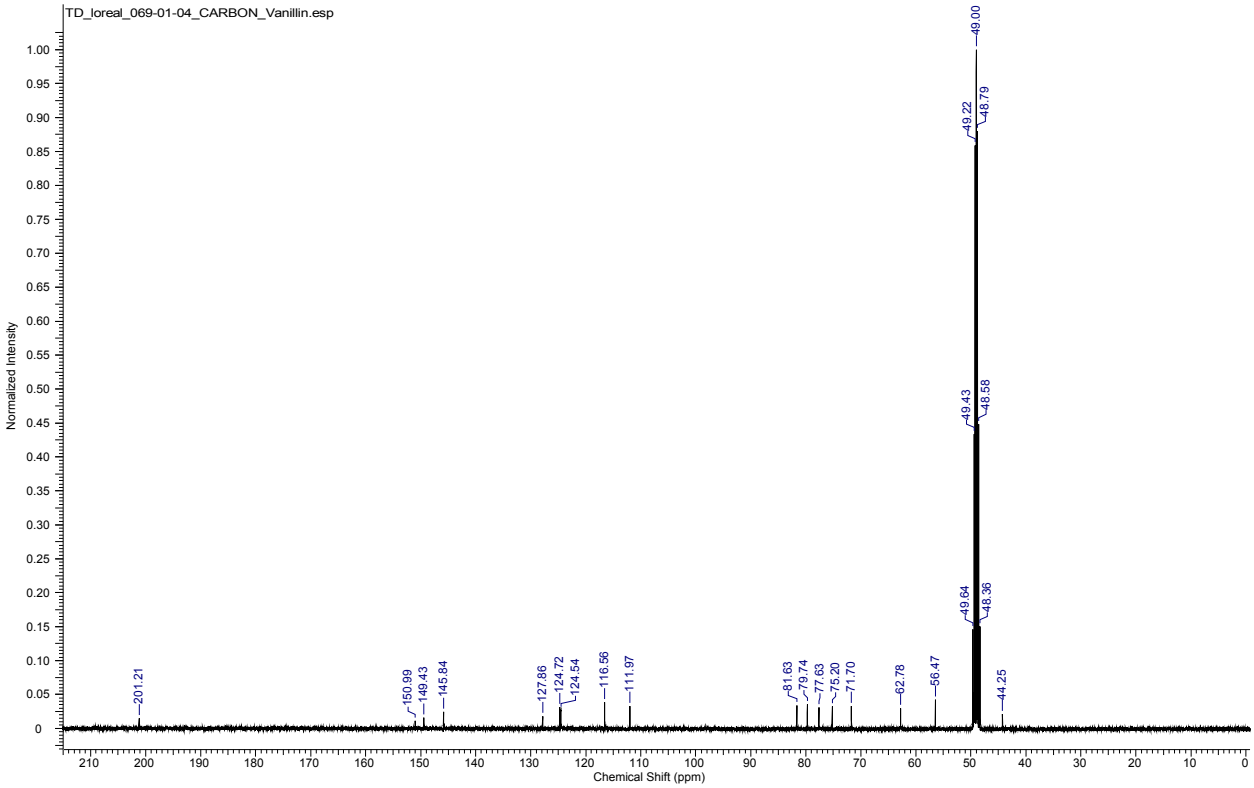

TD_loreal_065-02-03_PROTON_Furfural.esp
Normalized Intensity
Chemical Shift (ppm)
4.85
M11(dd)
M08(m)
M10(t)
M09(ddd)
3.31
M04(d)
M02(d)
M05(dd)
M01(d)
M03(d)
M06(m)
M07(dd)
M12(dd)
7.65
7.47
7.43
6.85
6.84
6.71
6.67
6.58
6.57
6.57
3.78
3.78
3.75
3.63
3.61
3.36
3.35
3.16
3.14
3.09
3.06
3.05
2.88
2.86
0.72 0.95 0.80 0.87 0.78
1.95 1.07 1.64 1.01 0.93 0.95 1.00

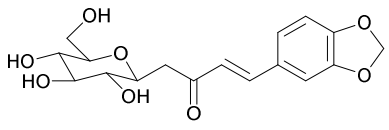

TD_loreal_065-02-03_CARBON_Furfural.esp
Normalized Intensity
Chemical Shift (ppm)
49.00
200.63
152.46
146.86
131.09
124.61
117.52
113.76
81.63
79.73
77.54
75.14
71.68
62.75
44.32


OH
HO
HO
O
OH
O
OH
O

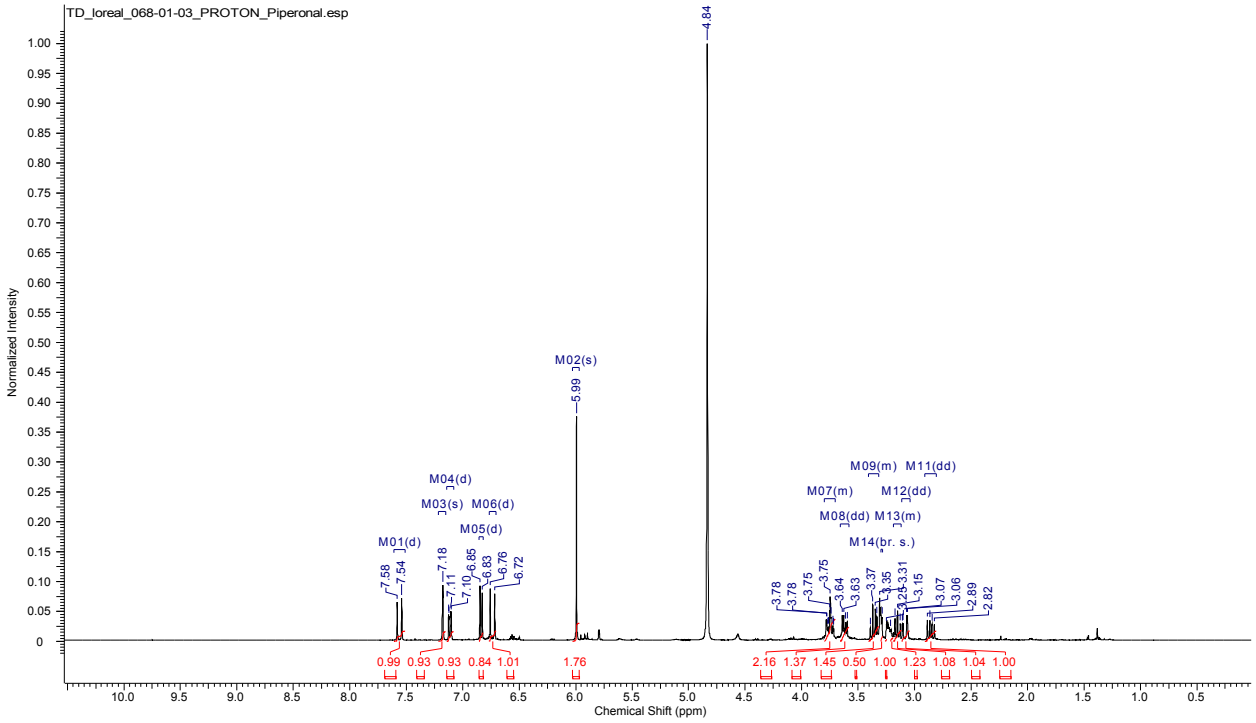
2e

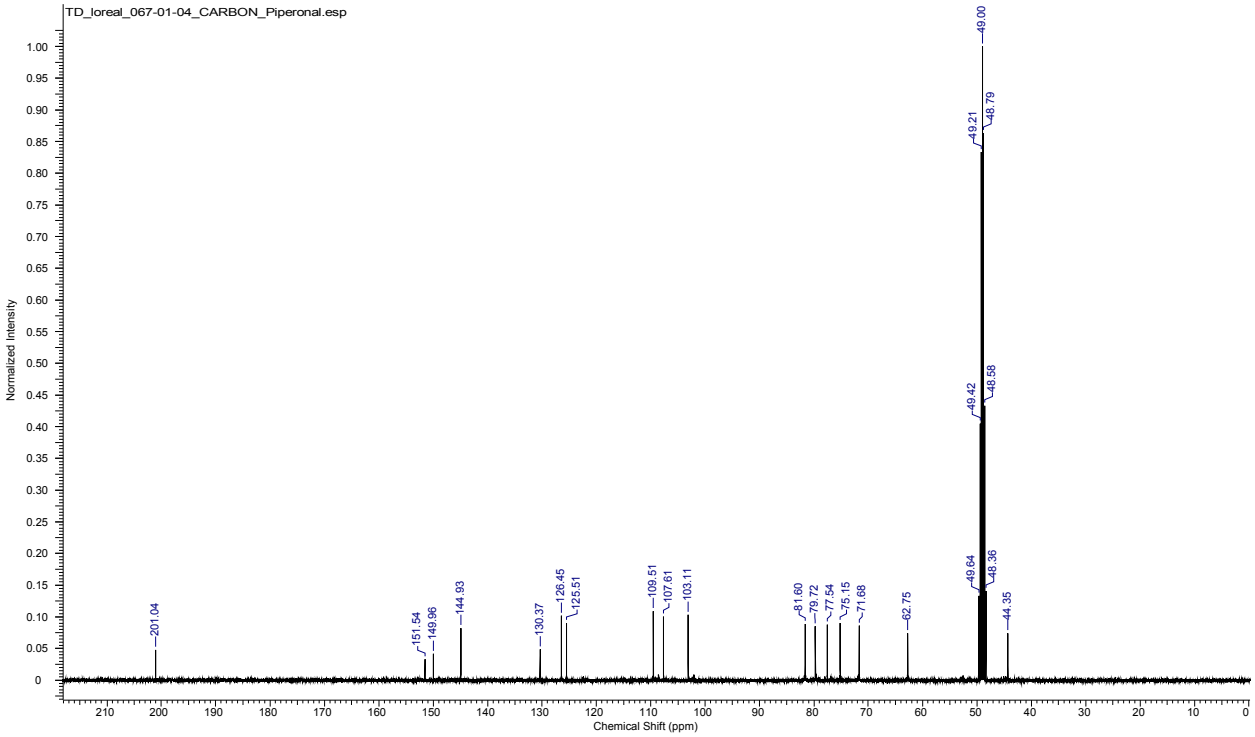

TD_loreal_069-01-04_PROTON_Vanillin.esp
Normalized Intensity
Chemical Shift (ppm)
4.85
M07(m)
M06(m)
M09(m)
M12(dd)
M10(m)
M11(t)
M05(d)
M03(dd)
M02(d)
M04(d)
M01(d)
M08(dd)
M13(dd)
3.90
3.31
7.63
7.59
7.24
7.13
7.13
6.84
6.81
6.79
6.75
3.92
3.76
3.76
3.64
3.37
3.18
3.15
3.13
3.09
3.08
2.90
2.88
1.04 0.96 1.00 0.97 1.00
2.96 2.37 1.26 1.48 1.18 1.98 1.01

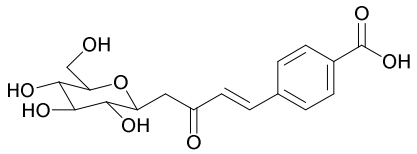

TD_loreal_069-01-04_CARBON_Vanillin.esp
Normalized Intensity
Chemical Shift (ppm)
49.00
48.79
49.22
49.43
48.58
49.64
48.36
201.21
150.99
149.43
145.84
127.86
124.72
124.54
116.56
111.97
81.63
79.74
77.63
75.20
71.70
62.78
56.47
44.25


OH
HO
HO
O
OH
O
O
O

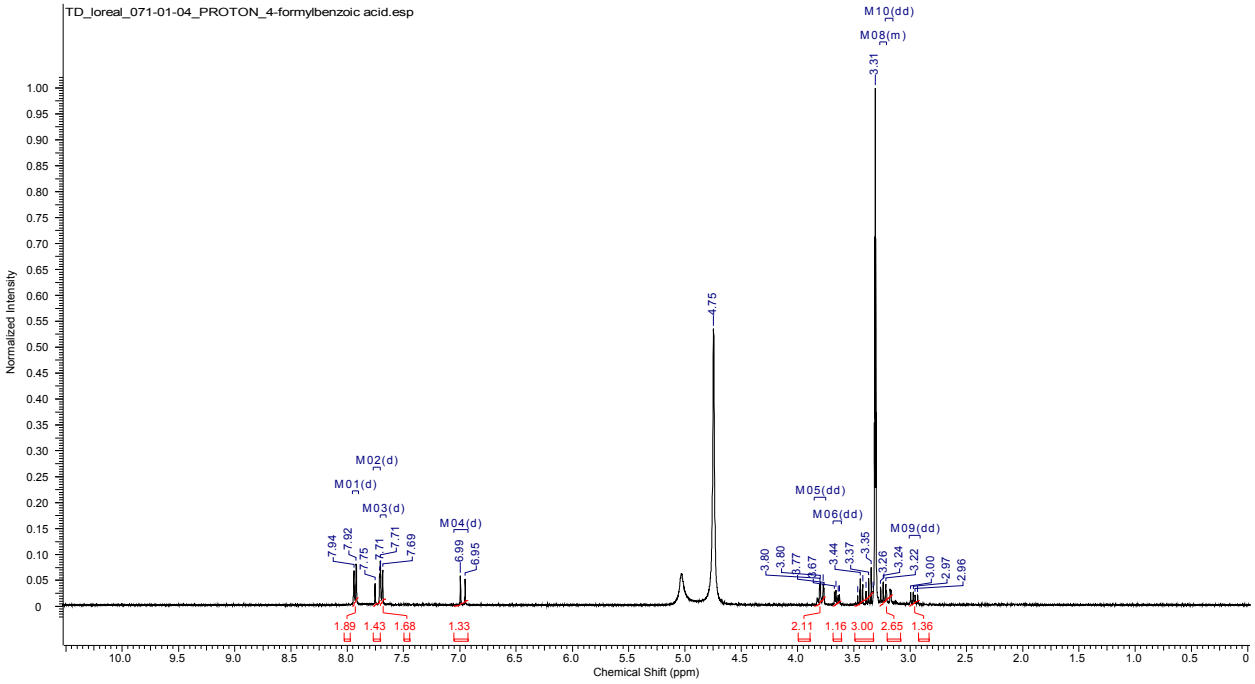
2f

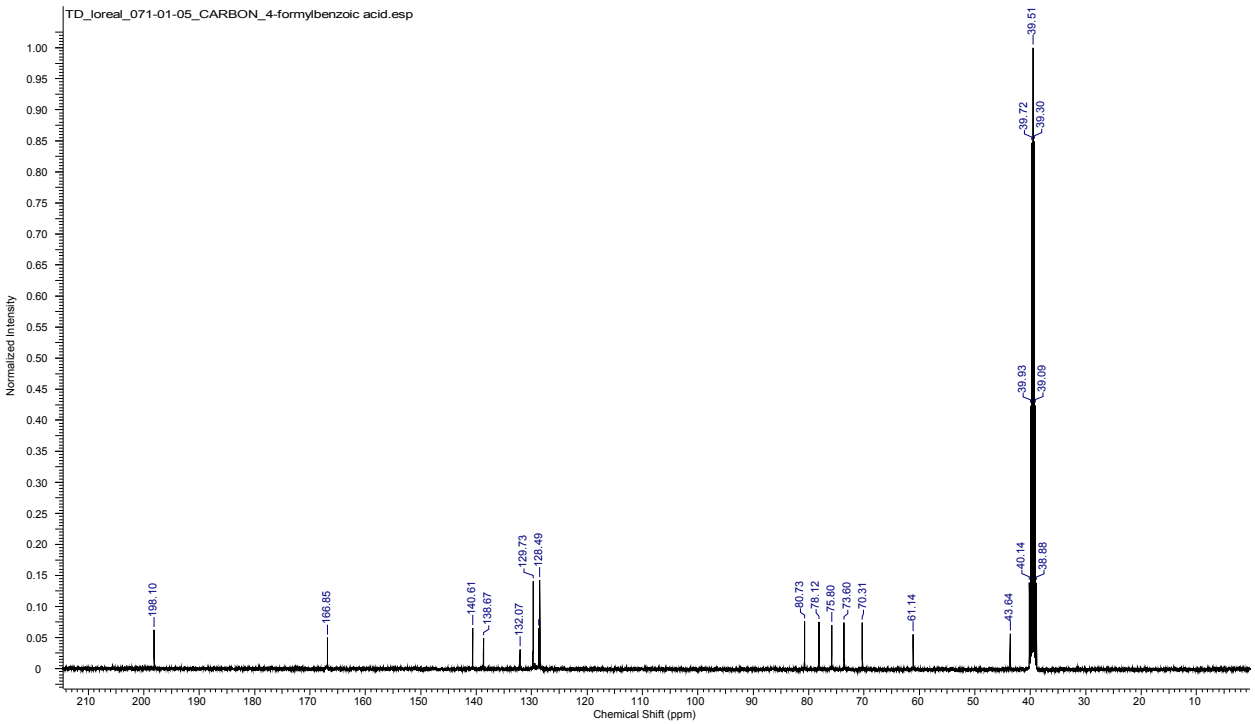

TD_loreal_068-01-03_PROTON_Piperonal.esp
Normalized Intensity
Chemical Shift (ppm)
4.84
5.99
M02(s)
M01(d)
M04(d)
M03(s)
M06(d)
M05(d)
M09(m)
M11(dd)
M07(m)
M12(dd)
M08(dd)
M13(m)
M14(br. s.)
0.99 0.93 0.93 0.84 1.01 1.76 2.16 1.37 1.45 0.50 1.00 1.23 1.08 1.04 1.00

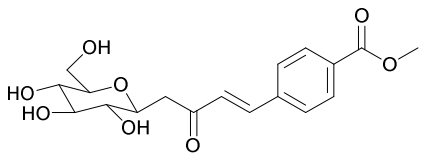

TD_loreal_067-01-04_CARBON_Piperonal.esp
Normalized Intensity
Chemical Shift (ppm)
49.00
48.79
49.21
49.42
48.58
49.64
48.36
201.04
151.54
149.96
144.93
130.37
126.45
125.51
109.51
107.61
103.11
81.60
79.72
77.54
75.15
71.68
62.75
44.35


OH
HO
HO
O
OH
O
O
OH

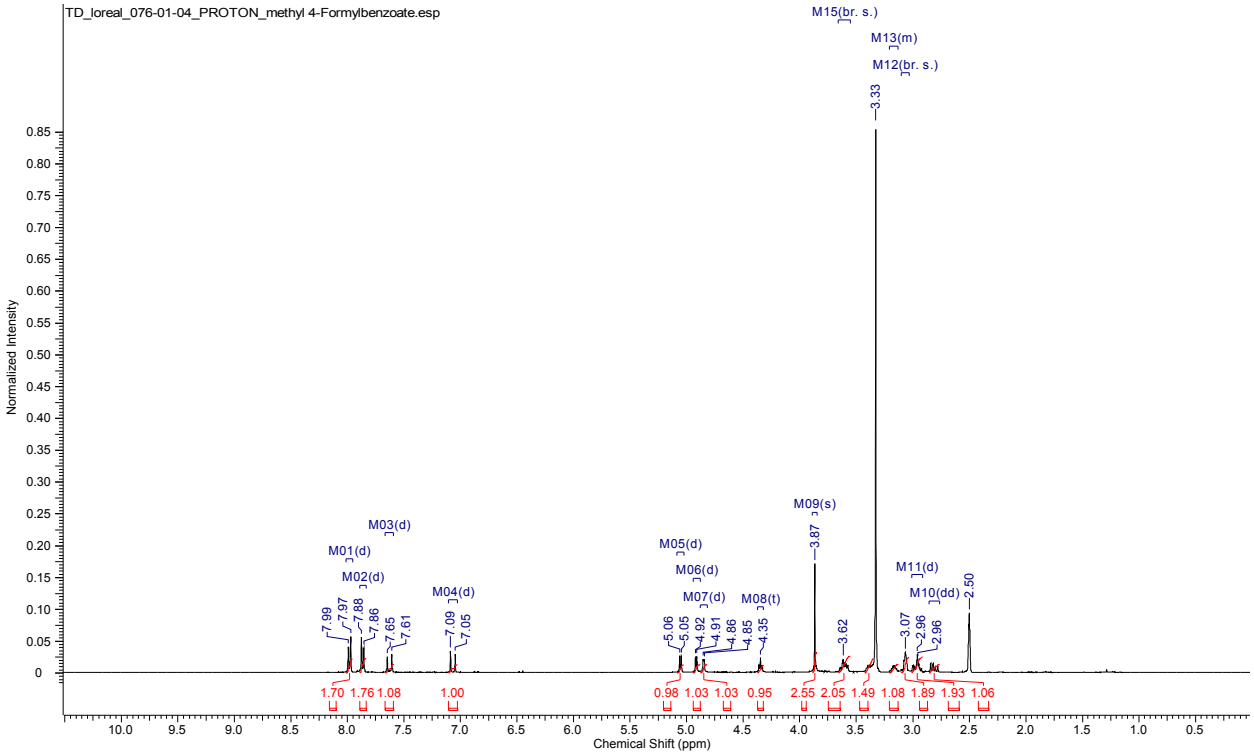
2g

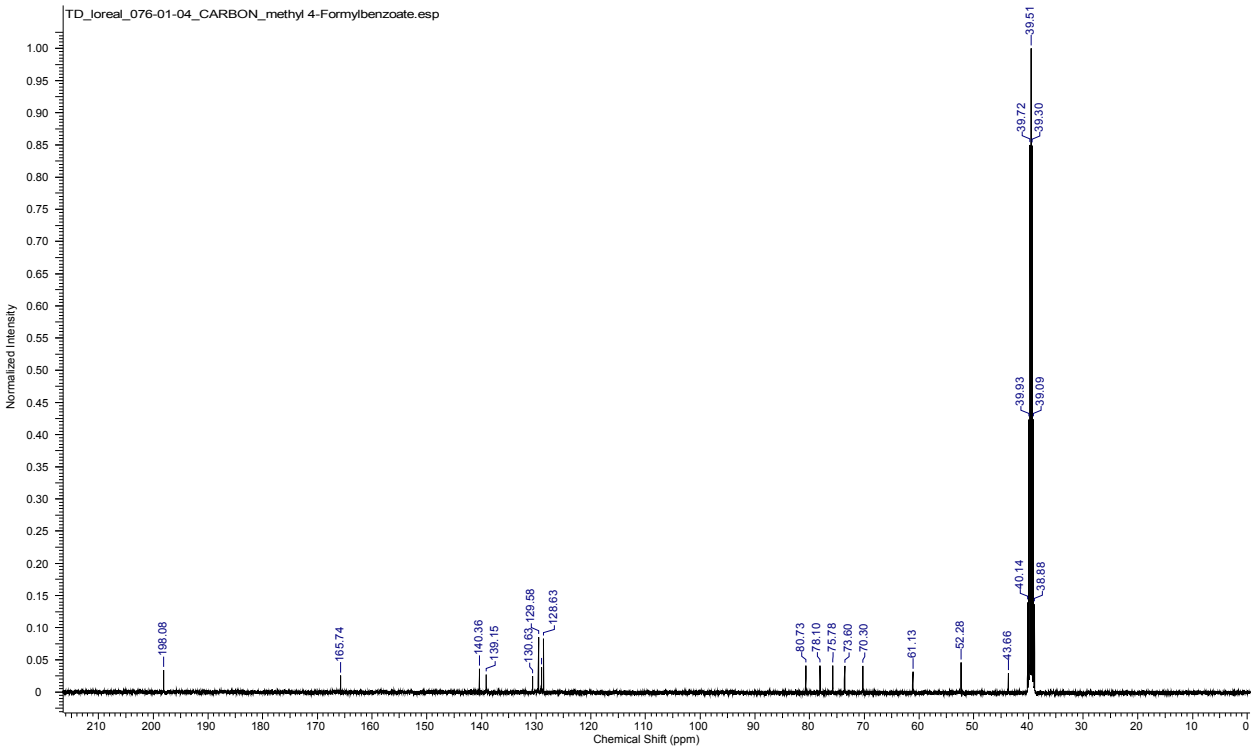

TD_loreal_071-01-04_PROTON_4-formylbenzoic acid.esp
M10(dd)
M08(m)
3.31
4.75
M02(d)
M01(d)
M03(d)
M04(d)
M05(dd)
M06(dd)
M09(dd)
7.94
7.92
7.75
7.71
7.71
7.69
6.99
6.95
3.80
3.80
3.77
3.67
3.44
3.37
3.35
3.26
3.24
3.22
3.00
2.97
2.96
1.89
1.43
1.68
1.33
2.11
1.16
3.00
2.65
1.36
Normalized Intensity
Chemical Shift (ppm)

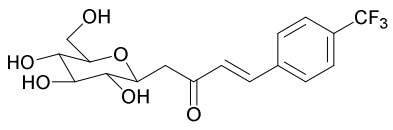

TD_loreal_071-01-05_CARBON_4-formylbenzoic acid.esp
39.51
39.72
39.30
39.93
39.09
40.14
38.88
198.10
166.85
140.61
138.67
132.07
129.73
128.49
80.73
78.12
75.80
73.60
70.31
61.14
43.64
Normalized Intensity
Chemical Shift (ppm)


OH
HO
HO
O
OH
O
O
O

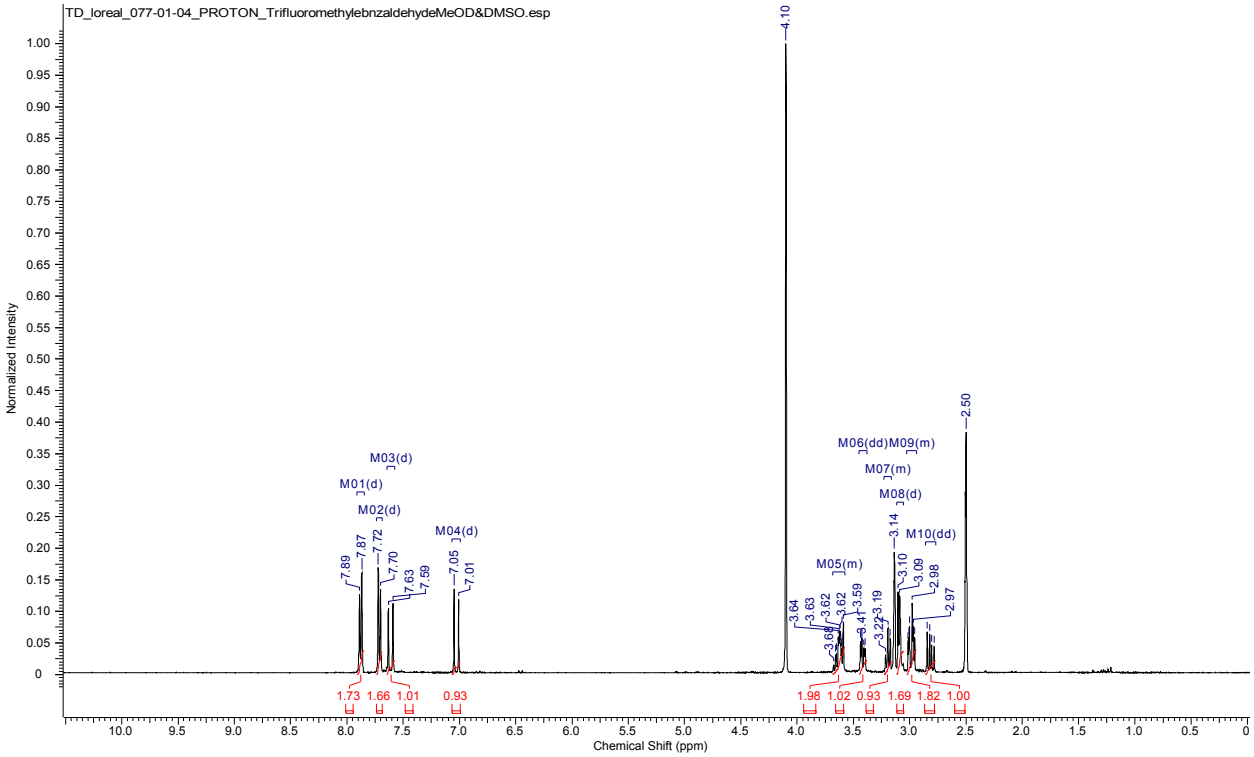
2h

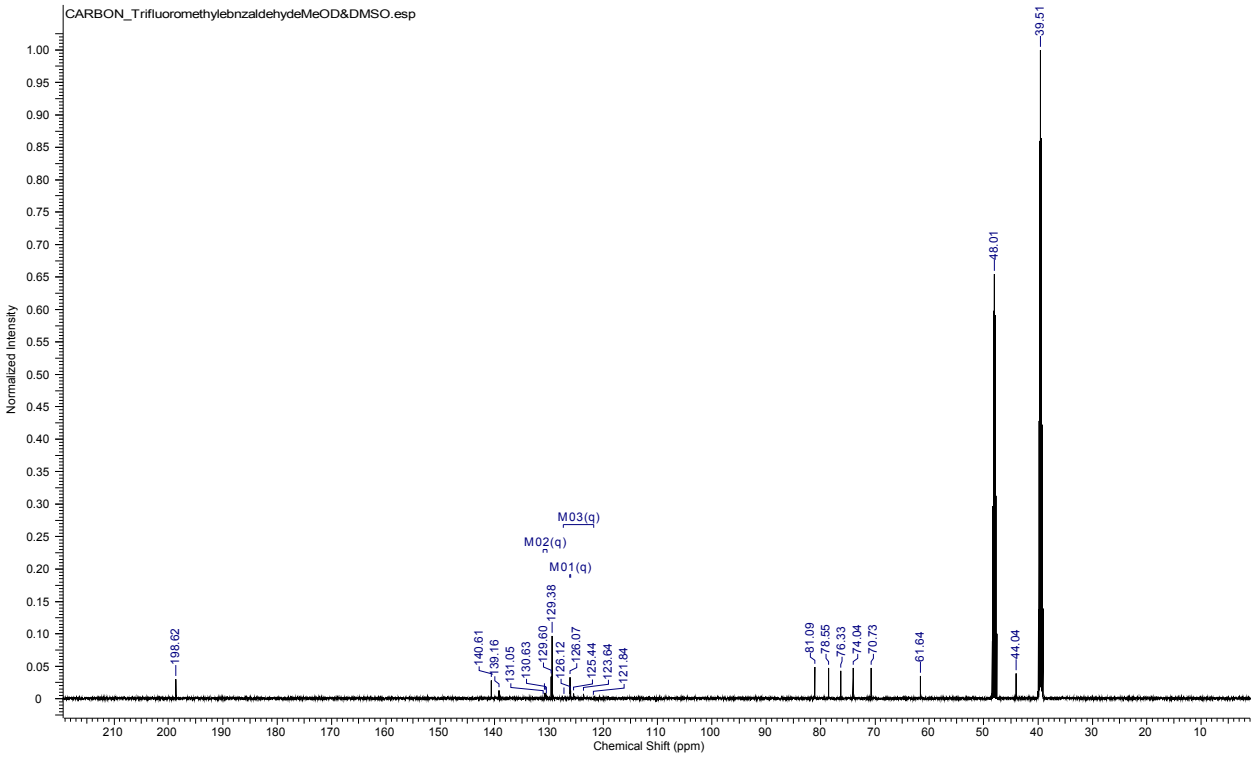

TD_loreal_076-01-04_PROTON_methyl 4-Formylbenzoate.esp
M15(br. s.)
M13(m)
M12(br. s.)
3.33
M09(s)
3.87
M03(d)
M01(d)
M02(d)
M04(d)
M05(d)
M06(d)
M07(d)
M08(t)
M11(d)
M10(dd)
2.50
7.99
7.97
7.88
7.86
7.65
7.61
7.09
7.05
5.06
5.05
4.92
4.91
4.86
4.85
4.35
3.62
3.07
2.96
2.96
1.70 1.76 1.08 1.00 0.98 1.03 1.03 0.95 2.55 2.05 1.49 1.08 1.89 1.93 1.06
Normalized Intensity
Chemical Shift (ppm)

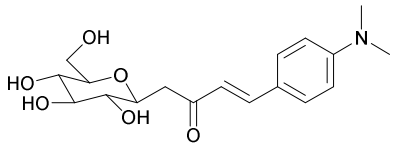

TD_loreal_076-01-04_CARBON_methyl 4-Formylbenzoate.esp
39.51
39.72
39.30
39.93
39.09
40.14
38.88
198.08
165.74
140.36
139.15
130.63
129.58
128.63
80.73
78.10
75.78
73.60
70.30
61.13
52.28
43.66
Normalized Intensity
Chemical Shift (ppm)


OH
HO
HO
O
OH
O
CF3

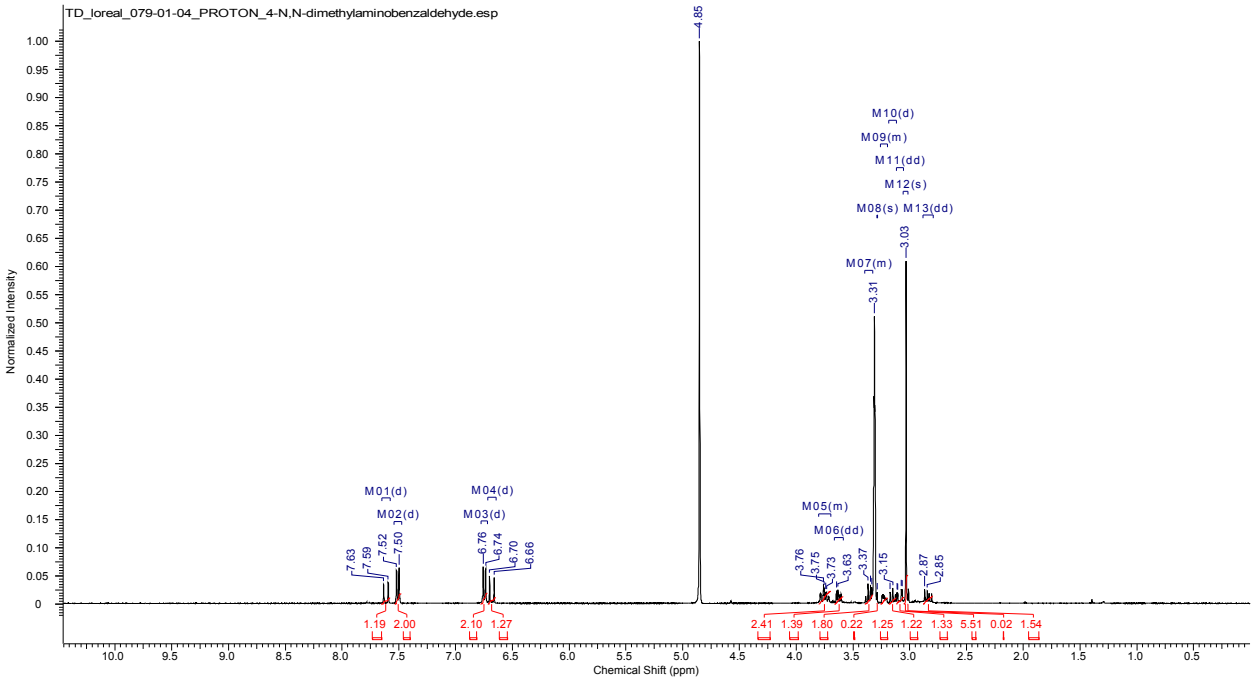
2i

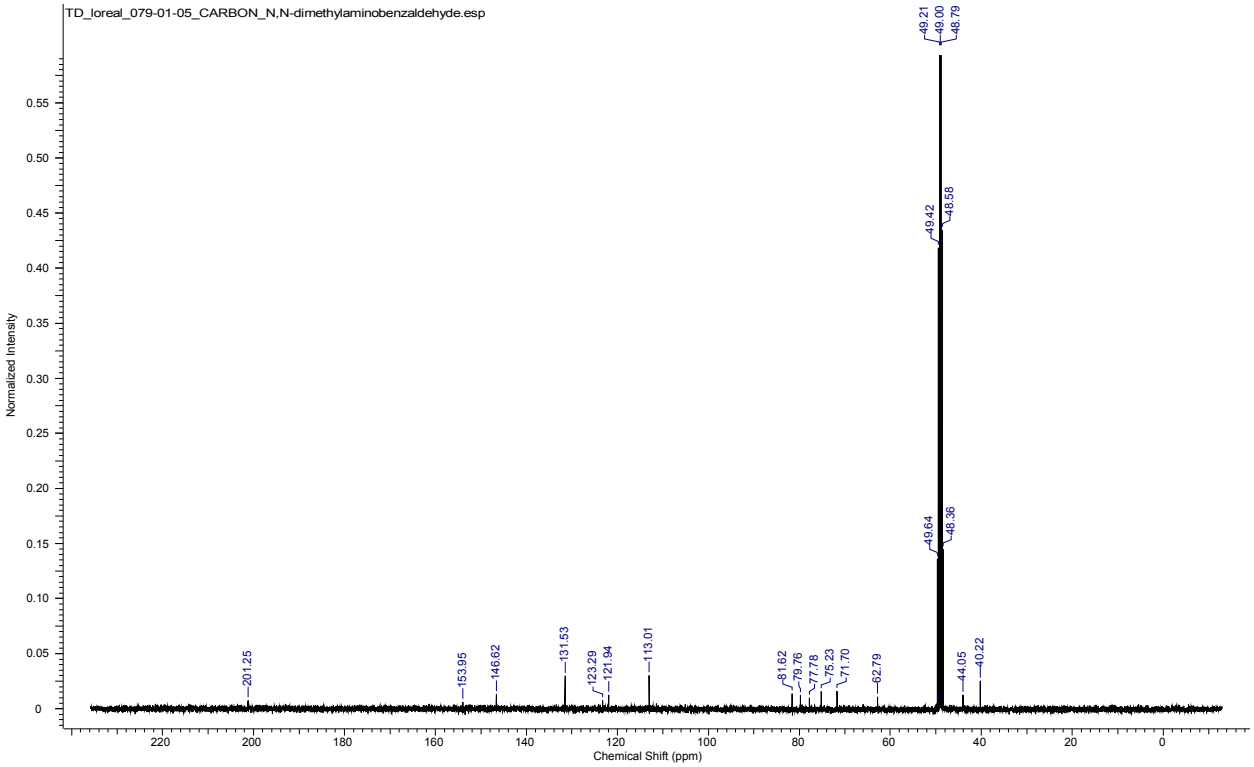

TD_loreal_077-01-04_PROTON_TrifluoromethylebnzaldehydeMeOD&DMSO.esp
Normalized Intensity
Chemical Shift (ppm)
M01(d)
M02(d)
M03(d)
M04(d)
M05(m)
M06(dd)M09(m)
M07(m)
M08(d)
M10(dd)
4.10
2.50
7.89
7.87
7.72
7.70
7.63
7.59
7.05
7.01
3.64
3.63
3.62
3.62
3.59
3.41
3.22
3.19
3.14
3.10
3.09
2.98
2.97
1.73
1.66
1.01
0.93
1.98
1.02
0.93
1.69
1.82
1.00

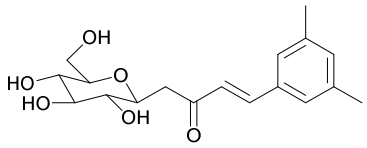

CARBON_TrifluoromethylebnzaldehydeMeOD&DMSO.esp
Normalized Intensity
Chemical Shift (ppm)
M01(q)
M02(q)
M03(q)
39.51
48.01
198.62
140.61
139.16
131.05
130.63
129.60
129.38
126.12
126.07
125.44
123.64
121.84
81.09
78.55
76.33
74.04
70.73
61.64
44.04


OH
HO
HO
O
OH
O
N

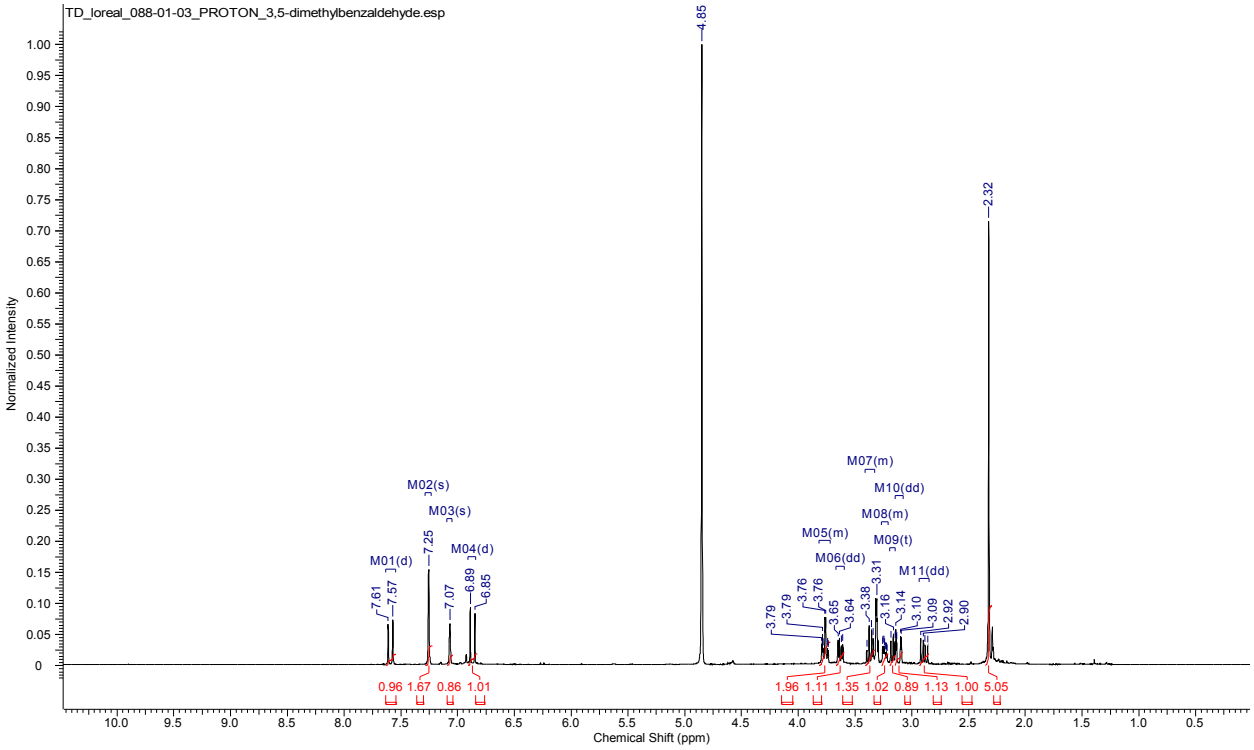
2j

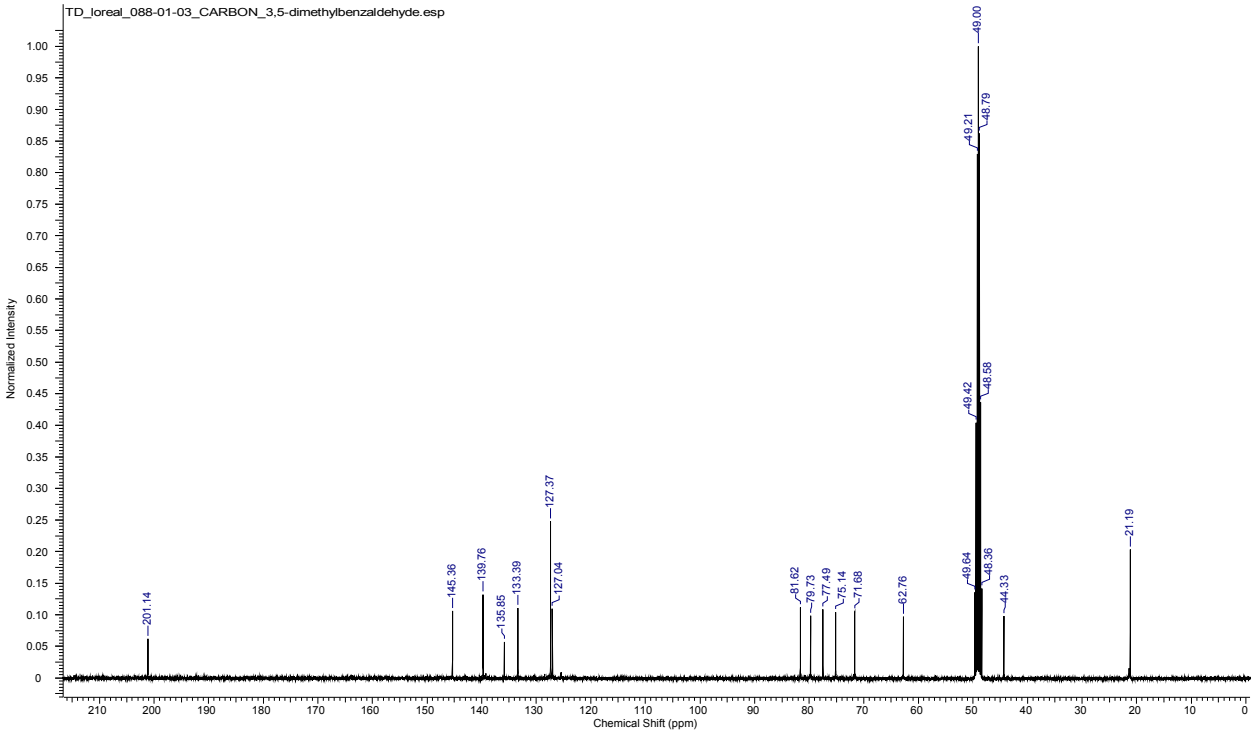

TD_loreal_079-01-04_PROTON_4-N,N-dimethylaminobenzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
4.85
M10(d)
M09(m)
M11(dd)
M12(s)
M08(s) M13(dd)
3.03
M07(m)
3.31
M01(d)
M02(d)
M04(d)
M03(d)
M05(m)
M06(dd)
7.63
7.59
7.52
7.50
6.76
6.74
6.70
6.66
3.76
3.75
3.73
3.63
3.37
3.15
2.87
2.85
1.19 2.00 2.10 1.27 2.41 1.39 1.80 0.22 1.25 1.22 1.33 5.51 0.02 1.54

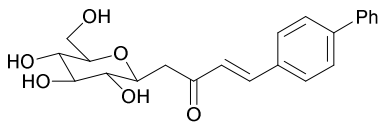

TD_loreal_079-01-05_CARBON_N,N-dimethylaminobenzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
49.21
49.00
48.79
49.42
48.58
49.64
48.36
201.25
153.95
146.62
131.53
123.29
121.94
113.01
81.62
79.76
77.78
75.23
71.70
62.79
44.05
40.22


OH
HO
HO
O
OH
O

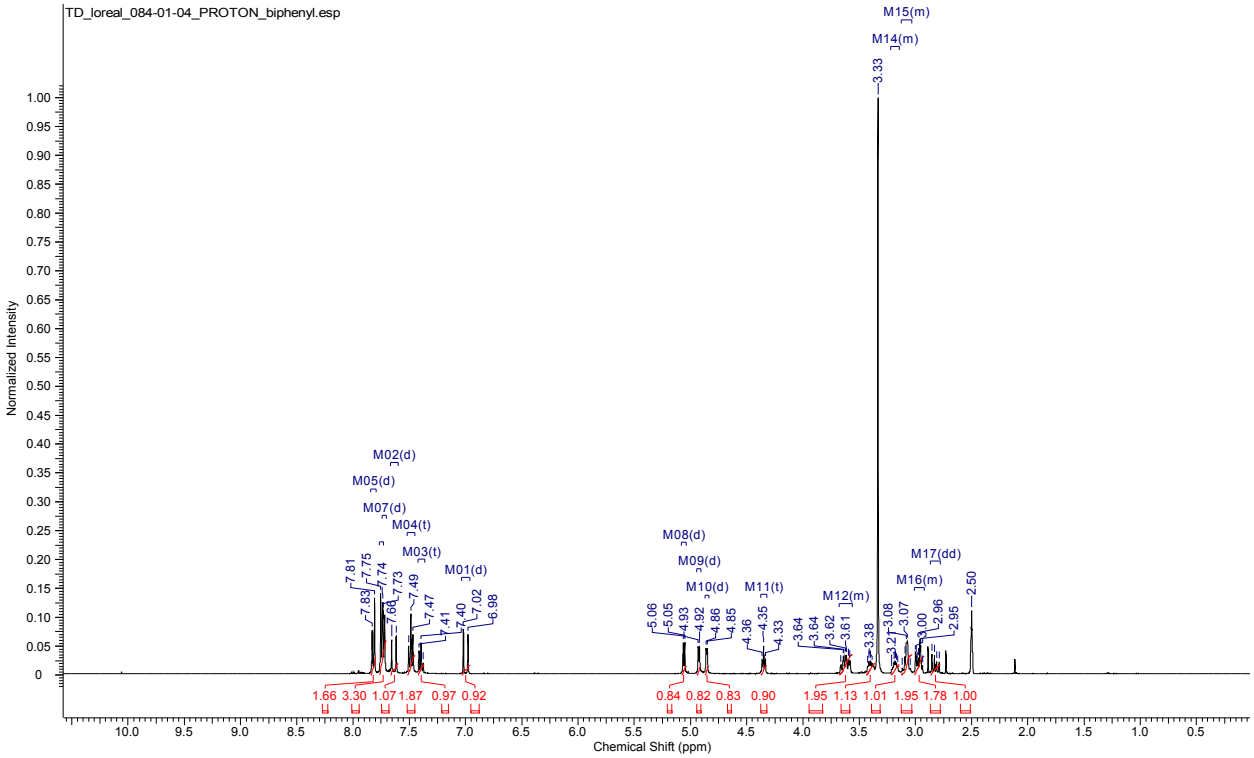
2k

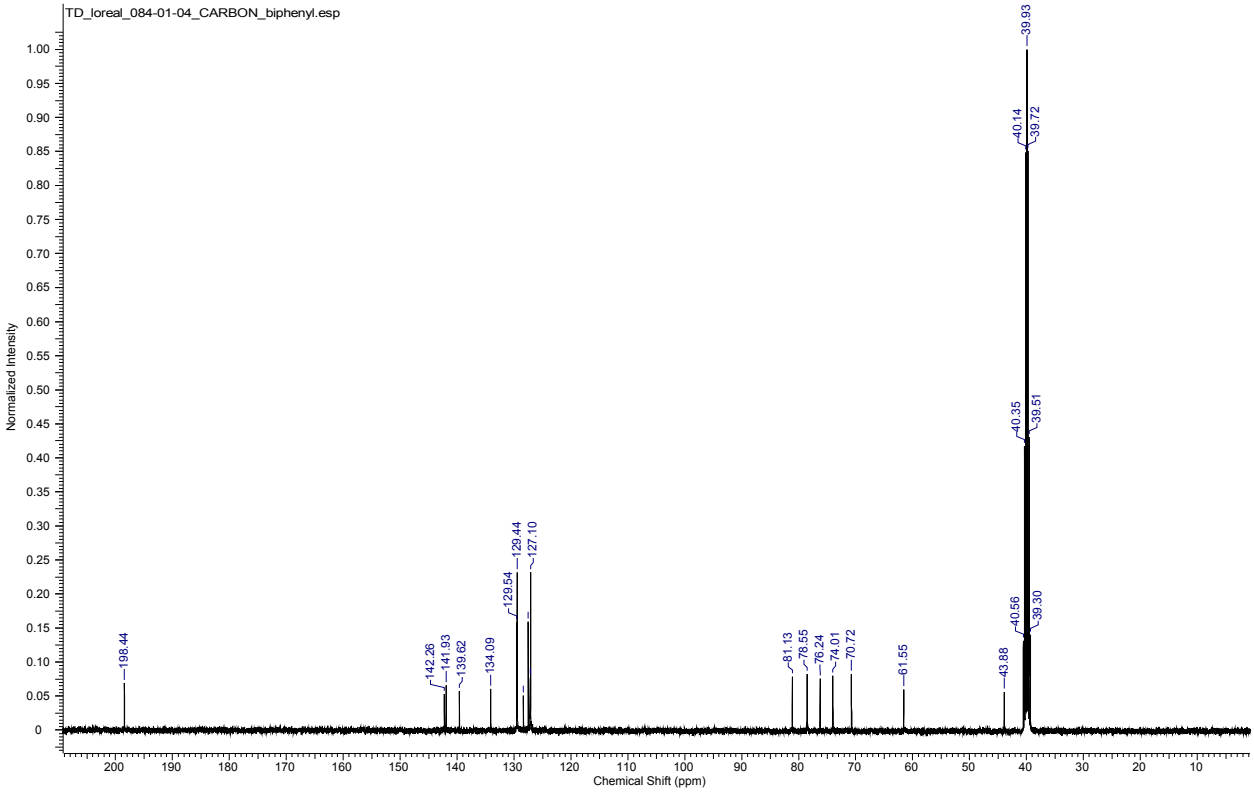

TD_loreal_088-01-03_PROTON_3,5-dimethylbenzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
4.85
2.32
M01(d)
M02(s)
M03(s)
M04(d)
M05(m)
M06(dd)
M07(m)
M08(m)
M09(t)
M10(dd)
M11(dd)
0.96 1.67 0.86 1.01
1.96 1.11 1.35 1.02 0.89 1.13 1.00 5.05

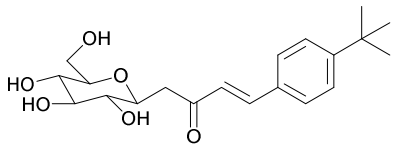

TD_loreal_088-01-03_CARBON_3,5-dimethylbenzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
201.14
145.36
139.76
135.85
133.39
127.37
127.04
81.62
79.73
77.49
75.14
71.68
62.76
49.64
49.42
49.21
49.00
48.79
48.58
48.36
44.33
21.19


OH
HO
HO
O
OH
O
Ph

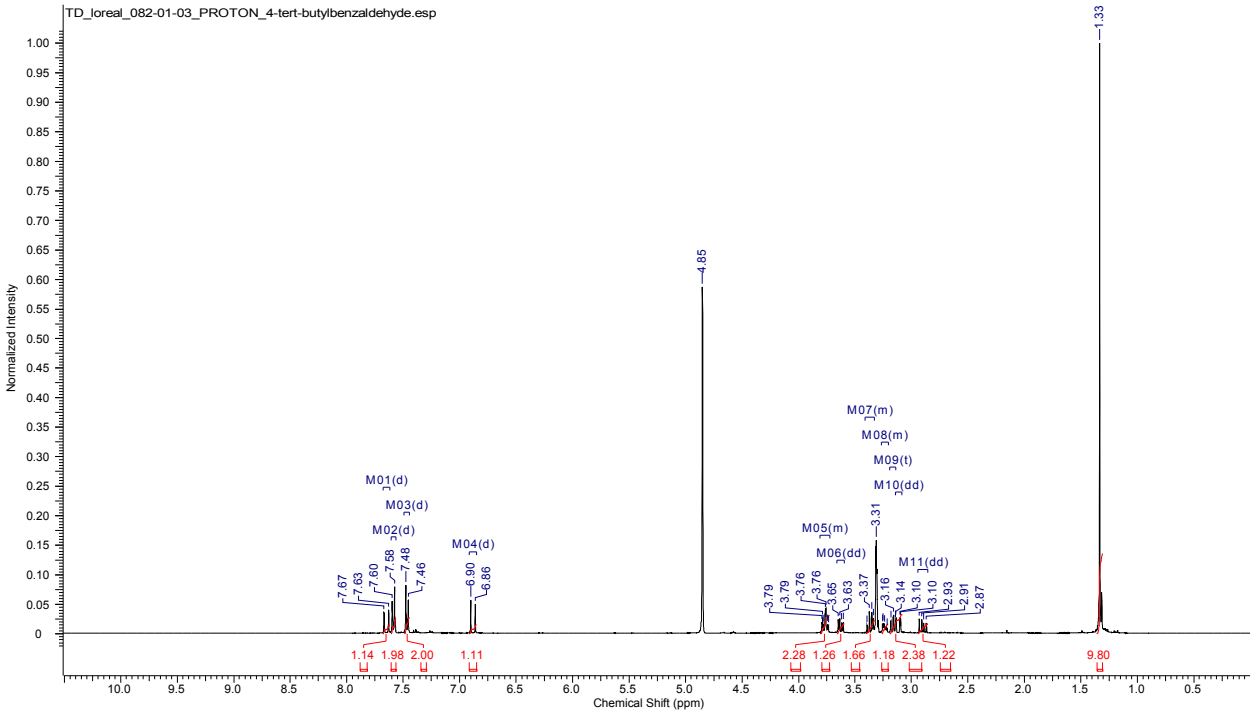
2l

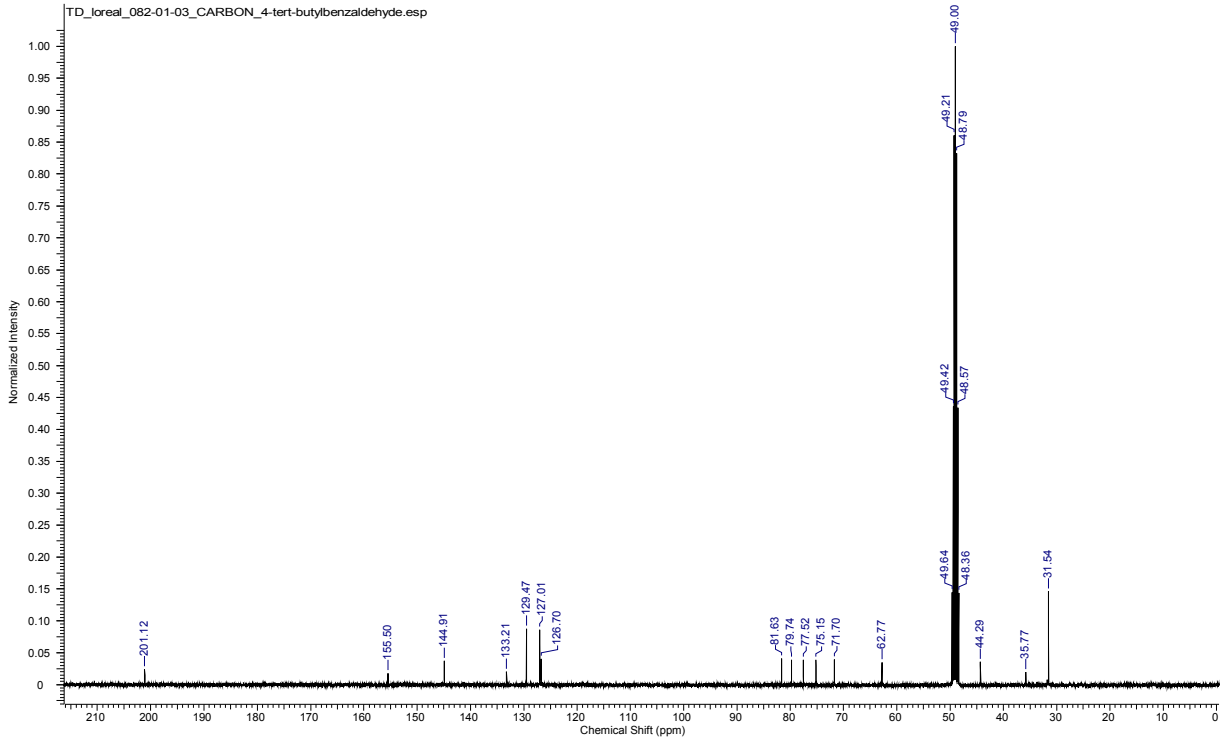

TD_loreal_084-01-04_PROTON_biphenyl.esp
Normalized Intensity
Chemical Shift (ppm)
M15(m)
M14(m)
3.33
M02(d)
M05(d)
M07(d)
M04(t)
M03(t)
M01(d)
M08(d)
M09(d)
M10(d)
M11(t)
M12(m)
M17(dd)
M16(m)
2.50
1.66 3.30 1.07 1.87 0.97 0.92
0.84 0.82 0.83 0.90
1.95 1.13 1.01 1.95 1.78 1.00

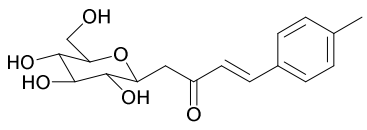

TD_loreal_084-01-04_CARBON_biphenyl.esp
Normalized Intensity
Chemical Shift (ppm)
39.93
40.14
39.72
40.35
39.51
40.56
39.30
198.44
142.26
141.93
139.62
134.09
129.54
129.44
127.10
81.13
78.55
76.24
74.01
70.72
61.55
43.88


OH
HO
HO
O
OH
O

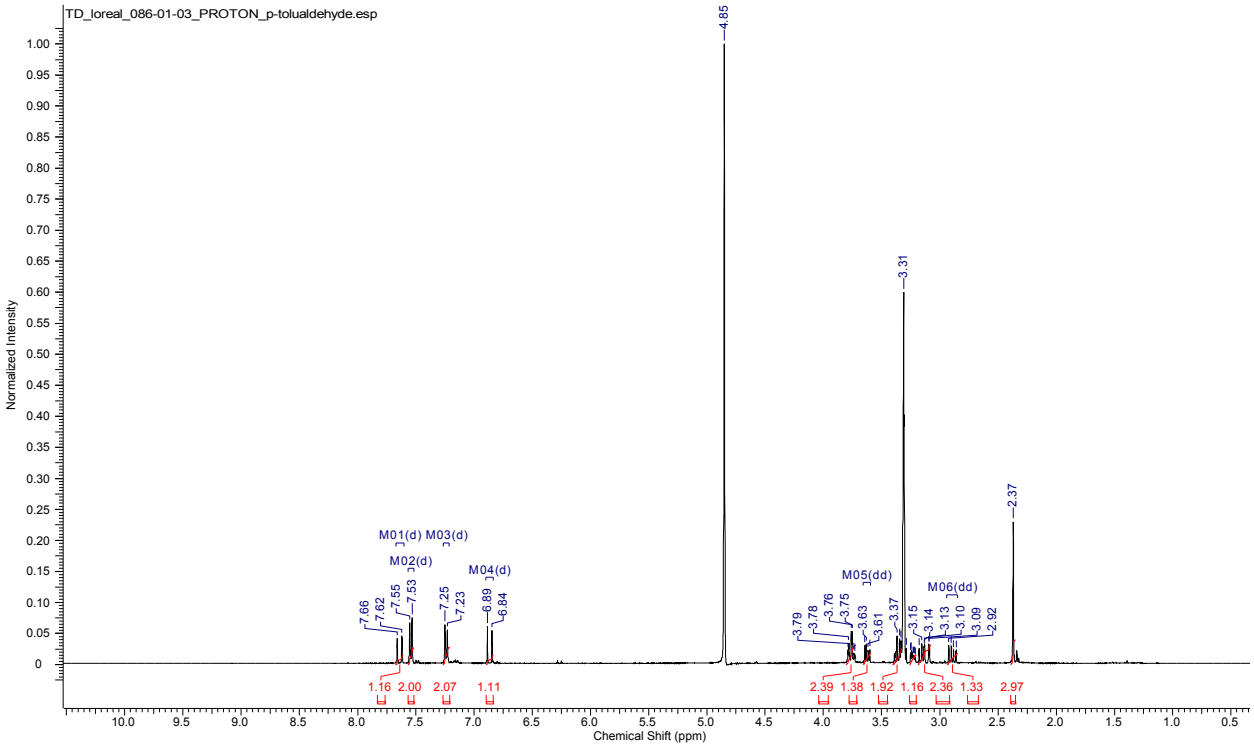
2m

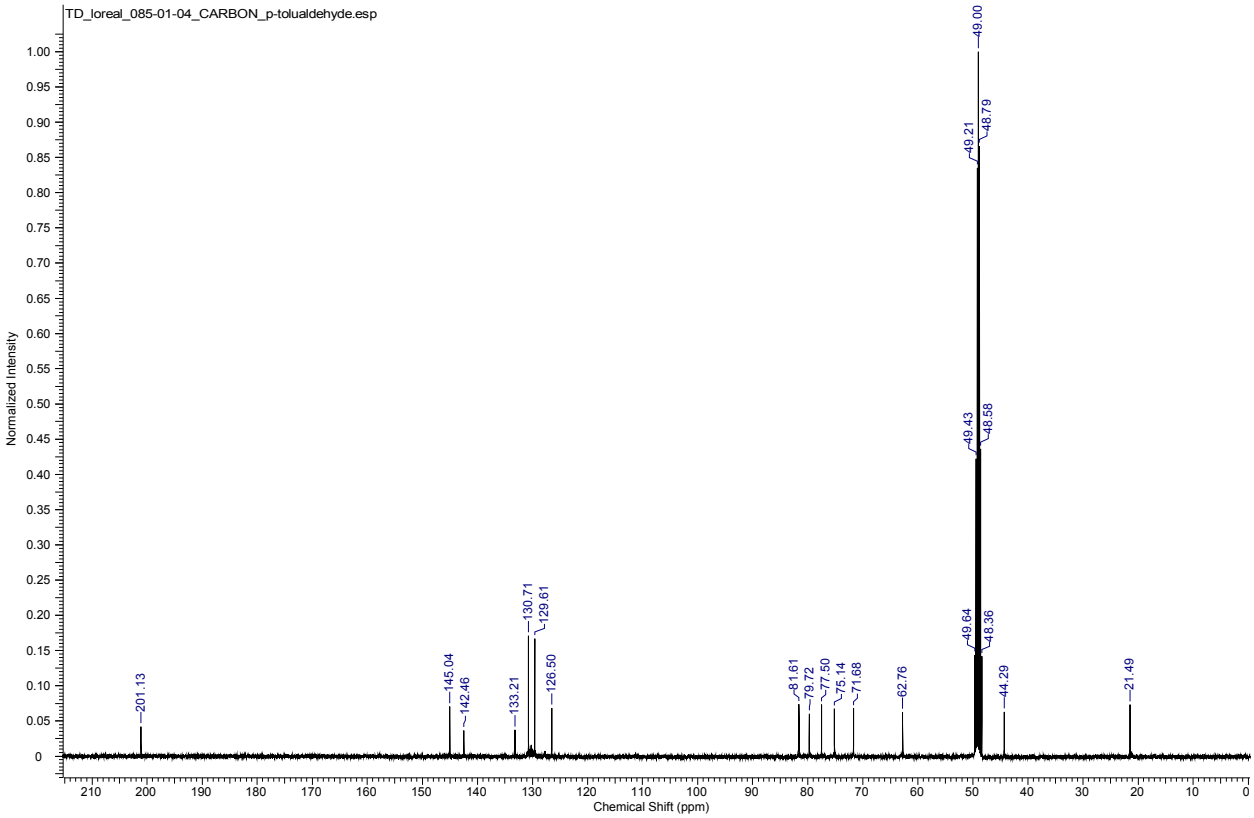

TD_loreal_082-01-03_PROTON_4-tert-butylbenzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)
M01(d)
M02(d)
M03(d)
M04(d)
M05(m)
M06(dd)
M07(m)
M08(m)
M09(t)
M10(dd)
M11(dd)
1.14 1.98 2.00 1.11 2.28 1.26 1.66 1.18 2.38 1.22 9.80


TD_loreal_082-01-03_CARBON_4-tert-butylbenzaldehyde.esp
Normalized Intensity
Chemical Shift (ppm)


OH
HO
HO
O
OH
O

2n


TD_loreal_086-01-03_PROTON_p-tolualdehyde.esp
Normalized Intensity
Chemical Shift (ppm)
4.85
3.31
2.37
M01(d)
M03(d)
M02(d)
M04(d)
M05(dd)
M06(dd)
7.66
7.62
7.55
7.53
7.25
7.23
6.89
6.84
3.79
3.78
3.76
3.75
3.63
3.61
3.37
3.15
3.14
3.13
3.10
3.09
2.92
1.16
2.00
2.07
1.11
2.39
1.38
1.92
1.16
2.36
1.33
2.97


TD_loreal_085-01-04_CARBON_p-tolualdehyde.esp
Normalized Intensity
Chemical Shift (ppm)
49.00
48.79
49.21
49.43
48.58
49.64
48.36
201.13
145.04
142.46
133.21
130.71
129.61
126.50
81.61
79.72
77.50
75.14
71.68
62.76
44.29
21.49