Electronic Supplementary Information for:

Synthesis and antibacterial evaluation of anziaic acid and analogues as topoisomerase I inhibitors

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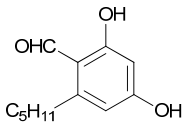
General

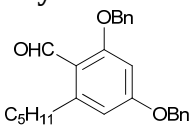
All reagents and solvents were obtained from Sigma-Aldrich (St. Louis, MO) and Fisher Scientific (Hanover Park, IL) and were used without further purification. Reactions were monitored either by thin-layer chromatography (TLC) or by a Shimadzu LC-20A series HPLC system. TLC was performed using glass plates pre-coated with silica gel (0.25 mm, 60-Å pore size, 230-400 mesh, Sorbent Technologies, GA) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV). Debenzylation reactions were done using domnick hunter NITROX UHP-60H hydrogen generator, USA. Flash column chromatography was performed using a Biotage Isolera One system and a Biotage SNAP cartridge. Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded employing a Bruker AM-400 spectrometer. Chemical shifts were expressed in parts per million (ppm), *J* values were in Hertz. Mass spectra were recorded on a Varian 500-MS IT mass spectrometer using ESI. High-resolution mass spectra (HRMS) were recorded with a BioTOF II ESI mass spectrometer. The purity of compounds was determined by analytical HPLC using a Gemini, 3µm, C18, 110Å column (50 mm × 4.6 mm, Phenomenex) and a flow rate of 1.0 mL/min. Gradient conditions: solvent A (0.1% trifluoroacetic acid in water) and solvent B (acetonitrile): 0-2.00 min 100% A, 2.00-7.00 min 0-100% B (linear gradient), 7.00-8.00 min 100% B, 8.00-9.00 min 0-100% A (linear gradient), 9.00-10.00 min 100% A, UV detection at 254 and 220 nm.

Synthesis of 2,4-dihydroxy-6-pentylbenzaldehyde (2)



To a stirred solution of $POCl_3$ (2.8 mL, 30 mmol) in dry DMF (8 mL) at 0 °C was slowly added a solution of olivetol (**1**) (2.18 g, 12 mmol) in dry DMF (6 mL). The mixture was allowed to stir at room temperature for 18 h. The reaction mixture was then cooled to 0 °C and cautiously treated with ice water (15 mL) and with 20% aqueous solution of NaOH to pH = 10. The resulting mixture was heated to reflux for 10 min and then allowed to cool to room temperature. The solution was then acidified to pH = 1 with concentrated hydrochloric acid, extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with brine (40 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane : Ethyl Acetate = 90 : 10) to give **2** as a yellow solid (1.42 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 12.44 (s, 1 H), 10.02 (s, 1 H), 7.27 (br, 1 H), 6.28 (d, *J* = 2.0 Hz, 1 H), 6.25 (d, *J* = 1.6 Hz, 1 H), 2.80 (t, *J* = 8.0 Hz, 3 H), 1.63-1.58 (m, 2 H), 1.36-1.31 (m, 4H), 0.89 (t, *J* = 6.4 Hz, 3 H); MS (ESI$^-$): m/z 207.2[M-H]$^-$; HPLC purity: 84.1% (254 nm), t_R: 7.02 min; 95.4% (220 nm), t_R: 7.02 min.

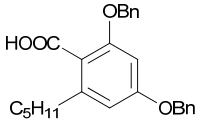
Synthesis of 2,4-bis(benzyloxy)-6-pentylbenzaldehyde



To a stirred solution of 2,4-dihydroxy-6-pentylbenzaldehyde **2** (1.423 g, 6.8 mmol) in acetone (20 mL) was added potassium carbonate (2.819 g, 20.4 mmol) and benzyl

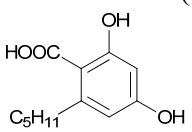
bromide (2.43 mL, 20.4 mmol) at room temperature. The mixture was then heated to reflux for 12 h and allowed to cool to room temperature. The solvent was removed under reduced pressure. The residue was dissolved in water (40 mL), extracted with ethyl acetate (2 × 25 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hexane : Ethyl Acetate = 97 : 3) to give an oil (1.861 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.56 (s, 1 H), 7.40-7.33 (m, 10 H), 6.47 (d, *J* = 2.4 Hz, 1 H), 6.44 (d, *J* = 2.4 Hz, 1 H), 5.08 (s, 4 H), 2.96 (t, *J* = 7.6 Hz, 2 H), 1.55-1.53 (m, 2 H), 1.36-1.33 (m, 4 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ190.31, 164.51, 163.53, 149.71, 136.15, 136.12, 128.77, 128.74, 128.36, 128.25, 127.61, 127.35, 117.36, 109.32, 97.86, 70.72, 70.20, 34.59, 31.96, 30.90, 22.64, 14.11; MS (ESI$^+$): m/z 411.3 $[M+Na]^+$; HPLC purity: 100% (254 nm), t_R: 8.30 min; 100% (220 nm), t_R: 8.30 min.

Synthesis of 2,4-bis(benzyloxy)-6-pentylbenzoic acid (**3**)



To a stirred solution of 2,4-bis(benzyloxy)-6-pentylbenzaldehyde (1.86 g, 4.8 mmol) and NaH_2PO_4 (1.36 g, 12 mmol) in DMSO (16 mL) and water (4 mL) at 0 °C was slowly added a solution of $NaClO_2$ (1.44 g, 12 mmol) in water (4 mL). The mixture was allowed to stir at room temperature for 14 h. The saturated aqueous solution (20 mL) of Na_2CO_3 was added. The mixture was then acidified to pH ≈ 1 with concentrated hydrochloric acid and extracted with ethyl acetate (2 × 25 mL). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was first purified by flash column chromatography (hexane : ethyl acetate = 80 : 20) to give a mixture of the desired product and trace amount of starting material. The mixture was then recrystallized in hexane/ethyl acetate (95 : 5) to give the pure product as a white solid (1.182 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41-7.29 (m, 10 H), 6.50 (d, *J* = 2.0 Hz, 1 H), 6.48 (d, *J* = 2.0 Hz, 1 H), 5.10 (s, 2 H), 5.04 (s, 2 H), 2.79 (t, *J* = 8.0 Hz, 2 H), 1.62-1.58 (m, 2 H), 1.33-1.29 (m, 4 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 170.48, 161.09, 158.06, 146.58, 136.35, 135.94, 128.74, 128.73, 128.27, 128.23, 127.61, 127.28, 114.23, 108.82, 98.67, 71.25, 70.19, 34.68, 31.78, 31.07, 22.51, 14.06; MS (ESI$^-$): m/z 403.4 $[M-H]^-$ HPLC purity: 98.9% (254 nm), t_R: 7.66 min; 99.3% (220 nm), t_R: 7.66 min.

Synthesis of 2,4-dihydroxy-6-pentylbenzoic acid (**4**)

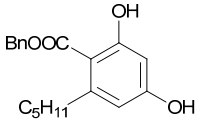


Method A: To a stirred solution of 2,4-dihydroxy-6-pentylbenzaldehyde **2** (833 mg, 4 mmol) and NaH_2PO_4 (1.20 g, 10 mmol) in DMSO (10 mL) and water (2.5 mL) at 0 °C was slowly added a solution of $NaClO_2$ (1.13 g, 10 mmol) in water (2.5 mL). The mixture was allowed to stir at room temperature for 14 h. The saturated aqueous solution (15 mL) of Na_2CO_3 was added. The mixture was then acidified to pH ≈ 1 with concentrated hydrochloric acid and extracted with ethyl acetate (2 × 25 mL). The combined organic

layer was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : ethyl acetate = 70 : 30) to give the desired product (453 mg, 50%), which was used directly in the next step. HPLC purity: 96.5% (254 nm), t_R: 6.50 min; 95.2% (220 nm), t_R: 6.50 min.

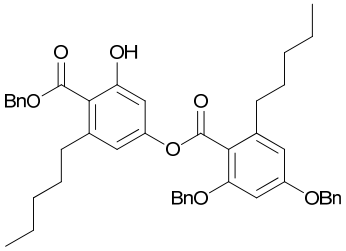
Method B: A solution of 2,4-bis(benzyloxy)-6-pentylbenzoic acid **3** (402 mg, 1 mmol) in ethyl acetate (4 mL) was treated with 10 wt% Pd/C (49 mg, 12 wt%). The mixture was stirred at room temperature under 1 bar H_2 atmosphere for 24 h. The mixture was then filtered through Celite and washed with ethyl acetate (2 × 10 mL). The combined organic layer was evaporated under reduced pressure to give the desired product (216 mg, 97%). ^{1}H NMR (400 MHz, d_6-DMSO, ppm) δ 10.08 (br, 1 H), 6.15 (d, J = 2.4 Hz, 1 H), 6.12 (d, J = 2.4 Hz, 1 H), 2.73 (t, J = 7.2 Hz, 2 H), 1.47-1.45 (m, 2 H), 1.26-1.24 (m, 4 H), 0.84 (t, 6.8 Hz, 3 H); ^{13}C NMR (100.5 MHz, d_6-DMSO, ppm) δ 173.20, 164.04, 162.02, 147.69, 110.49, 105.71, 101.02, 35.74, 31.79, 31.46, 22.36, 14.34; MS (ESI$^-$): m/z 223.3 $[M-H]^-$; HPLC purity: 100% (254 nm), t_R: 6.50 min; 100% (220 nm), t_R: 6.50 min.

Synthesis of benzyl 2,4-dihydroxy-6-pentylbenzoate (**5**)



A suspension of 2,4-dihydroxy-6-pentylbenzoic acid **4** (192 mg, 0.86 mmol), BnBr (102 μL, 0.86 mmol) and potassium bicarbonate (103 mg, 1.03 mmol) in DMF (4 mL) was stirred at ambient temperature for 5 h. The mixture was then quenched with water (20 mL), extracted with ethyl acetate (2 × 25 mL). The combined organic layer was washed with H_2O (20 mL) and brine (20 mL), then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : ethyl acetate = 85 : 15) to give **5** as a solid (247 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.82 (br, 1 H), 7.44-7.37 (m, 5 H), 6.28 (d, J = 2.4 Hz, 1 H), 6.20 (d, J = 2.4 Hz, 1 H), 5.77 (br, 1 H), 5.34 (s, 2 H), 2.75 (t, J = 8.0 Hz, 2 H), 1.39-1.37 (m, 2 H), 1.15-1.11 (m, 2 H), 1.04-1.02 (m, 2 H), 0.79 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 171.39, 165.39, 160.51, 149.19, 135.01, 129.06, 128.71, 110.88, 104.95, 101.40, 67.51, 36.98, 31.88, 31.82, 22.59, 14.03; MS (ESI$^+$): m/z 337.2 $[M+Na]^+$; HPLC purity: 99.7% (254 nm), t_R: 7.55 min; 97.7% (220 nm), t_R: 7.56 min.

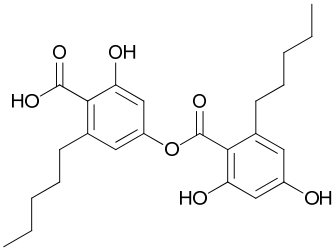
Synthesis of benzyl 4-((2,4-bis(benzyloxy)-6-pentylbenzoyl)oxy)-2-hydroxy-6-pentylbenzoate (6)



To a stirred solution of benzyl 2,4-dihydroxy-6-pentylbenzoate **5** (94.3 mg, 0.3 mmol) and 2,4-bis(benzyloxy)-6-pentylbenzoic acid **3** (121.4 mg, 0.3 mmol) in dry toluene (3

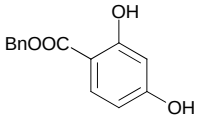
mL) was slowly added trifluoroacetic acid anhydride (486 μL, 3.45 mmol) at room temperature. The mixture was stirred overnight and the solvent was then removed under reduced pressure. The residue was purified by flash column chromatography (hexane : ethyl acetate = 97 : 3) to give **6** as a solid (135 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.45 (s, 1 H), 7.44-7.23 (m, 15 H), 6.63 (d, *J* = 2.0 Hz, 1 H), 6.50 (d, 2.4 Hz, 1 H), 6.48 (d, *J* = 2.0 Hz, 1 H), 6.38 (d, *J* = 2.4 Hz, 1 H), 5.36 (s, 2 H), 5.06 (s, 2 H), 5.05 (s, 2 H), 2.70-2.66 (m, 4 H), 1.66-1.62 (m, 2 H), 1.35-1.31 (m, 6 H), 1.14-1.10 (m, 2 H), 1.02-1.01 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3 H), 0.79 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 171.09, 166.06, 164.41, 161.02, 157.66, 155.27, 148.32, 143.94, 136.49, 136.35, 134.79, 129.10, 128.83, 128.78, 128.71, 128.57, 128.22, 128.11, 127.59, 127.54, 116.13, 115.62, 109.56, 108.78, 107.46, 98.24, 70.70, 70.20, 67.81, 36.84, 33.95, 31.92, 31.86, 31.71, 31.06, 22.60, 22.57, 14.08, 14.04; MS (ESI$^-$): m/z 699.6 [M-H]$^-$; HRMS (ESI$^+$) Calcd for $C_{45}H_{48}O_7$ (M^+): 701.3473, Found: 701.3472; HPLC purity: 100% (254 nm), t_R: 8.91 min; 100% (220 nm), t_R: 8.91 min.

Synthesis of anziaic acid



A solution of benzyl 4-((2,4-bis(benzyloxy)-6-pentylbenzoyl)oxy)-2-hydroxy-6-pentylbenzoate (**6**) (135 mg, 0.19 mmol) in ethyl acetate (5 mL) was treated with 10% Pd/C (38 mg). The mixture was stirred at room temperature under 1 bar of H_2 atmosphere for ca. 2 h. The reaction was stopped once it was complete (monitored by HPLC). The mixture was filtered through Celite and washed with ethyl acetate. The combined organic layer was evaporated under reduced pressure (the water bath temperature was kept below 30 °C) to give anziaic acid as a white solid (78.6 mg, 95%). ^{1}H NMR (400 MHz, CD_3OD, ppm) δ 6.62 (d, *J* = 2.4 Hz, 1 H), 6.56 (d, *J* = 2.0 Hz, 1 H), 6.27 (d, *J* = 2.0 Hz, 1 H), 6.22 (d, *J* = 2.4 Hz, 1 H), 2.92 (t, *J* = 7.2 Hz, 2 H), 2.86 (t, *J* = 7.6 Hz, 2 H), 1.62-1.60 (m, 4 H), 1.34-1.32 (m, 8 H), 0.91-0.86 (m, 6 H); ^{13}C NMR (100.5 MHz, CD_3OD, ppm) δ 173.89, 170.41, 166.05, 164.34, 164.14, 154.90, 149.36, 149.04, 116.22, 113.16, 112.23, 109.03, 105.22, 102.01, 37.73, 36.79, 33.21, 33.13, 32.99, 32.62, 23.60, 23.46, 14.44, 14.38; MS (ESI$^-$): m/z 429.3 [M-H]$^-$; HRMS (ESI$^+$) Calcd for $C_{24}H_{30}O_7$ (M+Na$^+$): 453.1884, Found: 453.1887; HPLC purity: 100% (254 nm), t_R: 7.54 min; 100% (220 nm), t_R: 7.54 min.

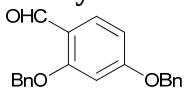
Synthesis of benzyl 2,4-dihydroxybenzoate (7)



Following the procedure for compound **5**: 2,4-dihydroxybenzoic acid (1.54 g, 10 mmol), benzyl bromide (1.25 mL, 10.5 mmol), potassium bicarbonate (1.2 g, 12 mmol), DMF (20 mL); Eluent (hexane : ethyl acetate = 85 : 15); Product: white solid (2.02 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.00 (br, 1 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.42-7.37 (m,

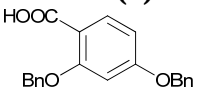
5 H), 6.40 (d, J = 2.4 Hz, 1 H), 6.35 (dd, J = 8.4, 2.4 Hz, 1 H), 5.62 (br, 1 H), 5.35 (s, 2 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 169.79, 163.72, 162.07, 135.50, 132.10, 128.72, 128.52, 128.25, 107.96, 105.96, 103.19, 66.76; MS (ESI$^-$): m/z 243.2[M-H]$^-$; HPLC purity: 100% (254 nm), t_R: 6.85 min; 97.1% (220 nm), t_R: 6.85 min.

Synthesis of 2,4-bis(benzyloxy)benzaldehyde



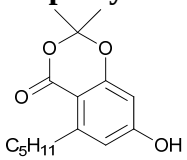
Following the procedure for compound 2,4-bis(benzyloxy)-6-pentylbenzaldehyde: 2,4-dihydroxybenzaldehyde (2.76 g, 20 mmol), benzyl bromide (5 mL, 42 mmol), potassium carbonate (6.08 g, 44 mmol), acetone (20 mL); Eluent (hexane : ethyl acetate = 95 : 5); Product: solid (6.12 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.38 (s, 1 H), 7.83 (d, J = 8.8 Hz, 1 H), 7.43-7.35 (m, 10 H), 6.63 (dd, J = 8.8, 1.6 Hz, 1 H), 6.59 (d, J = 2.0 Hz, 1 H), 5.12 (s, 2 H), 5.09 (s, 2 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 188.29, 165.22, 162.80, 135.98, 135.95, 130.54, 128.79, 128.78, 128.42, 128.34, 127.58, 127.32, 119.56, 107.07, 100.15, 70.50, 70.43; MS (ESI$^-$): m/z 317.2 [M-H]$^-$; HPLC purity: 98.7% (254 nm), t_R: 7.65 min; 98.7% (220 nm), t_R: 7.65 min.

Synthesis of 2,4-bis(benzyloxy)benzoic acid (9)



Following the procedure for compound **3**: 2,4-bis(benzyloxy)benzaldehyde (824 mg, 2.6 mmol), $NaClO_2$ (80%, 880 mg, 7.8 mmol), NaH_2PO_4 (936 mg, 7.8 mmol), DMSO/H_2O (10 mL/4 mL); Eluent (hexane : ethyl acetate = 85 : 15); Product: solid (663 mg, 76%, containing trace amounts of starting material), pure product can be obtained following recrystallization in hexane/ethyl acetate (3:1). ^{1}H NMR (400 MHz, d_6-DMSO, ppm) δ 7.72 (d, J = 8.4 Hz, 1 H), 7.51-7.30 (m, 10 H), 6.80 (d, J = 2.0 Hz, 1 H), 6.67 (dd, J = 8.8, 2.0 Hz, 1 H), 5.19 (s, 2 H), 5.15 (s, 2 H); ^{13}C NMR (100.5 MHz, d_6-DMSO, ppm) δ 167.03, 163.01, 159.86, 137.40, 136.95, 133.69, 128.98, 128.83, 128.52, 128.35, 128.11, 127.51, 114.01, 106.79, 101.64, 70.12, 70.05; MS (ESI$^-$): m/z 333.3 [M-H]$^-$; HPLC purity: 100% (254 nm), t_R: 7.17 min; 100% (220 nm), t_R: 7.16 min.

Synthesis of 7-hydroxy-2,2-dimethyl-5-pentyl-4H-benzo[d][1,3]dioxin-4-one (12)

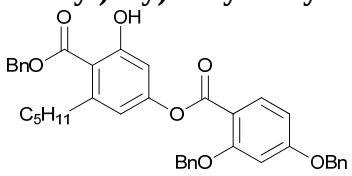


To a stirred solution of 2,4-dihydroxy-6-pentylbenzoic acid **4** (340 mg, 2 mmol), DMAP (14.9 mg, 0.12 mmol) and acetone (176 μL, 2.4 mmol) in DME (5 mL) was added thionyl chloride (190 μL, 2.6 mmol) at 0 ^{o}C. The mixture was allowed to warm to room temperature for 2 h. The mixture was then quenched with $NaHCO_3$ (aq, 30mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic layer was washed with brine (40 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : ethyl acetate = 80 : 20) to give **12** as a solid (164 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.35 (s, 1 H),

6.52 (d, J = 2.4 Hz, 1 H), 6.37 (d, J = 2.4 Hz, 1 H), 3.02 (t, J = 8.0 Hz, 2 H), 1.69 (s, 6 H), 1.63-1.56 (m, 2 H), 1.38-1.34 (m, 4 H), 0.87 (t, J = 7.2 Hz, 3 H); HPLC purity: 89.7% (254 nm), t_R: 7.05 min; 90.2% (220 nm), t_R: 7.05 min.

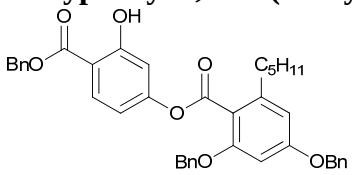
Synthesis of dimeric precursors 10a-d and 13

benzyl 4-((2,4-bis(benzyloxy)benzoyl)oxy)-2-hydroxy-6-pentylbenzoate (10a)



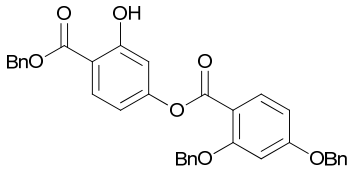
Following the procedure for compound **6**: compound **5** (62.9 mg, 0.2 mmol), compound **9** (70.2 mg, 0.21 mmol), trifluoroacetic acid anhydride (324 µL, 2.3 mmol), toluene (2 mL); Eluent (hexane : ethyl acetate = 97 : 3), then recrystallization from hexane if necessary; Product: white solid (79 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.48 (s, 1 H), 8.02 (d, J = 8.8 Hz, 1 H), 7.47-7.26 (m, 15 H), 6.73 (d, J = 2.4 Hz, 1 H), 6.65 (d, J = 2.0 Hz, 1 H), 6.61 (dd, J = 8.8, 2.0 Hz, 1 H), 6.54 (d, J = 2.0 Hz, 1 H), 5.36 (s, 2 H), 5.13 (s, 2 H), 5.08 (s, 2 H), 2.78 (t, J = 8.0 Hz, 2 H), 1.43-1.39 (m, 2 H), 1.14-1.13 (m, 2 H), 1.04-1.03 (m, 2 H), 0.79 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 171.15, 164.45, 164.14, 162.96, 161.14, 155.58, 148.18, 136.35, 136.08, 134.87, 134.71, 129.12, 128.82, 128.79, 128.61, 128.38, 127.90, 127.60, 126.96, 116.34, 111.73, 109.29, 108.93, 106.30, 101.34, 70.62, 70.36, 67.79, 36.90, 31.95, 31.90, 22.62, 14.08; MS (ESI$^+$): m/z 631.2 $[M+H]^+$; HRMS (ESI$^+$) Calcd for $C_{40}H_{38}O_7$ ($M+H^+$): 631.2691, Found: 631.2688; HPLC purity: 100% (254 nm), t_R: 8.56 min; 100% (220 nm), t_R: 8.56 min.

4-((benzyloxy)carbonyl)-3-hydroxyphenyl 2,4-bis(benzyloxy)-6-pentylbenzoate (10b)



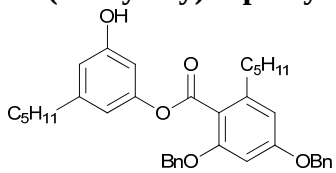
Following the procedure for compound **6**: compound **7** (48.4 mg, 0.2 mmol), compound **3** (84.4 mg, 0.21 mmol), trifluoroacetic acid anhydride (324 µL, 2.3 mmol), toluene (2 mL); Eluent (hexane : ethyl acetate = 97 : 3), then recrystallization from hexane if necessary; Product: white solid (107 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.88 (s, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.42-7.31 (m, 15 H), 6.75 (d, J = 2.0 Hz, 1 H), 6.61 (dd, J = 8.8, 2.0 Hz, 1 H), 6.49 (s, 1 H), 6.48 (s, 1 H), 5.36 (s, 2 H), 5.05 (s, 2 H), 5.04 (s, 2 H), 2.68 (t, J = 7.6 Hz, 2 H), 1.66-1.64 (m, 2 H), 1.32-1.31 (m, 4 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 169.55, 166.06, 163.15, 161.15, 157.76, 156.89, 144.03, 136.53, 136.37, 135.36, 131.24, 128.79, 128.74, 128.65, 128.30, 128.25, 128.19, 127.61, 127.49, 115.51, 113.44, 110.82, 110.24, 107.57, 98.32, 70.73, 70.23, 67.06, 33.99, 31.73, 31.08, 22.60, 14.09; MS (ESI$^+$): m/z 653.0 $[M+Na]^+$; HRMS (ESI$^+$) Calcd for $C_{40}H_{38}O_7$ ($M+H^+$): 631.2691, Found: 631.2691; HPLC purity: 100% (254 nm), t_R: 8.63 min; 100% (220 nm), t_R: 8.63 min.

benzyl 4-((2,4-bis(benzyloxy)benzoyl)oxy)-2-hydroxybenzoate (10c)



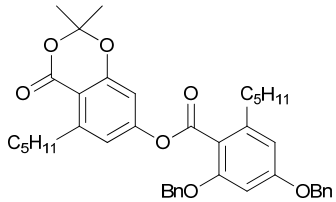
Following the procedure for compound **6**: compound **7** (70.5 mg, 0.29 mmol), compound **9** (96.8 mg, 0.29 mmol), trifluoroacetic acid anhydride (410 μL, 2.9 mmol), toluene (3 mL); Eluent (hexane : ethyl acetate = 97 : 3), then recrystallization from hexane if necessary; Product: white solid (105 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.89 (s, 1 H), 8.04 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.8 Hz, 1 H), 7.49-7.28 (m, 15 H), 6.84 (s, 1 H), 6.73 (d, *J* = 8.8 Hz, 1 H), 6.65 (s, 1 H), 6.63 (d, *J* = 9.2 Hz, 1 H), 5.38 (s, 2 H), 5.15 (s, 2 H), 5.10 (s, 2 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 169.60, 164.21, 163.08, 162.89, 161.21, 157.07, 136.29, 136.02, 135.33, 134.75, 131.13, 128.80, 128.78, 128.63, 128.42, 128.32, 127.93, 127.62, 126.90, 113.69, 111.48, 110.94, 109.96, 106.27, 101.31, 70.58, 70.38, 67.04; MS (ESI$^-$): m/z 559.4 $[M-H]^-$; HPLC purity: 100% (254 nm), t_R: 8.27 min; 100% (220 nm), t_R: 8.27 min.

3-hydroxy-5-pentylphenyl 2,4-bis(benzyloxy)-6-pentylbenzoate (10d)



Following the procedure for compound **6**: compound **8** (olivetol **1**) (43 mg, 0.24 mmol), compound **3** (81 mg, 0.2 mmol), trifluoroacetic acid anhydride (324 μL, 2.3 mmol), toluene (2 mL); Eluent (hexane : ethyl acetate = 97 : 3); Product: solid (65 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43-7.31 (m, 10 H), 6.50-6.47 (m, 3 H), 6.42 (s, 1 H), 6.25 (s, 1 H), 5.11 (br, 1 H), 5.06 (s, 2 H), 5.05 (s, 2 H), 2.69 (t, *J* = 7.6 Hz, 2 H), 2.45 (t, *J* = 7.6 Hz, 2 H), 1.65-1.64 (m, 2 H), 1.54-1.50 (m, 2 H), 1.33-1.28 (m, 8 H), 0.89-0.88 (m, 6 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 167.20, 160.88, 157.60, 156.26, 151.68, 145.74, 143.68, 136.54, 128.71, 128.60, 128.20, 128.06, 127.96, 127.60, 116.14, 113.95, 113.12, 107.43, 106.57, 98.22, 70.75, 70.21, 35.75, 33.93, 31.71, 31.51, 31.01, 30.67, 22.58, 22.53, 14.05; MS (ESI$^+$): m/z 589.3 $[M+Na]^+$; HRMS (ESI$^+$) Calcd for $C_{37}H_{42}O_5$ ($M+H^+$): 567.3105, Found: 567.3107; HPLC purity: 98.8% (254 nm), t_R: 8.44 min; 98.7% (220 nm), t_R: 8.44 min.

2,2-dimethyl-4-oxo-5-pentyl-4H-benzo[d][1,3]dioxin-7-yl 2,4-bis(benzyloxy)-6-pentyl benzoate (13)

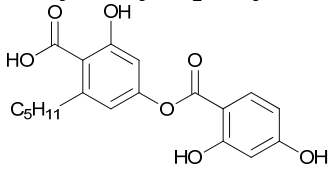


Following the procedure for compound **6**: compound **12** (38 mg, 0.14 mmol), compound **3** (61.7 mg, 0.15 mmol), trifluoroacetic acid anhydride (233 μL, 1.65 mmol), toluene (2 mL); Eluent (hexane : ethyl acetate = 97 : 3); Product: solid (80 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41-7.32 (m, 10 H), 6.60 (s, 1 H), 6.59 (s, 1 H), 6.52 (s, 1 H), 6.50

(s, 1 H), 5.07 (s, 2 H), 5.06 (s, 2 H), 3.00 (t, J = 7.6 Hz, 2 H), 2.69 (t, J = 7.6 Hz, 2 H), 1.69 (s, 6 H), 1.65-161 (m, 2 H), 1.53-1.51 (m, 2 H), 1.34-1.33 (m, 8 H), 0.90-0.88 (m, 6 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 165.90, 161.21, 159.71, 158.16, 157.84, 155.93, 150.46, 144.08, 136.44, 136.28, 128.72, 128.59, 128.24, 128.19, 127.65, 127.57, 118.42, 115.27, 109.51, 108.59, 107.57, 105.20, 98.26, 70.79, 70.23, 34.46, 33.93, 31.86, 31.68, 31.06, 30.61, 25.70, 22.56, 22.52, 14.07, 14.03; MS (ESI^+): m/z 673.4 $[M+Na]^+$; HRMS (ESI^+) Calcd for $C_{41}H_{46}O_7$ ($M+H^+$): 651.3317, Found: 651.3318; HPLC purity: 97.7% (254 nm), t_R: 8.79 min; 97.2% (220 nm), t_R: 8.79 min.

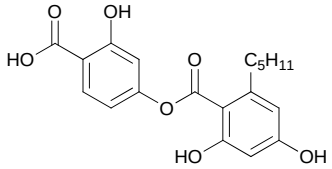
Synthesis of anziaic acid analogues 11a-d and 14

4-((2,4-dihydroxybenzoyl)oxy)-2-hydroxy-6-pentylbenzoic acid (11a)



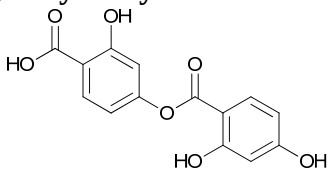
Following the procedure for anziaic acid: Compound **10a** (79 mg, 0.12 mmol), 10 wt% Pd/C (25 mg, 31 wt%), ethyl acetate (4 mL); Product: solid (45 mg, 100%). ^{1}H NMR (400 MHz, CD_3OD, ppm) δ 7.87 (d, J = 8.8 Hz, 1 H), 6.65 (d, J = 2.4 Hz, 1 H), 6.60 (d, J = 2.0 Hz, 1 H), 6.42 (dd, J = 8.8, 2.4 Hz, 1 H), 6.35 (d, J = 2.4 Hz, 1 H), 2.92 (t, J = 7.2 Hz, 2 H), 1.62-1.61 (m, 2 H), 1.37-1.35 (m, 4 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100.5 MHz, CD_3OD, ppm) δ 167.89, 165.25, 164.29, 162.61, 153.72, 147.55, 131.94, 114.96, 111.90, 108.30, 107.69, 103.39, 102.29, 35.39, 31.66, 31.29, 22.09, 12.98; MS (ESI^-): m/z 359.1 $[M-H]^-$; HPLC purity: 100% (254 nm), t_R: 6.96 min; 100% (220 nm), t_R: 6.96 min.

4-((2,4-dihydroxy-6-pentylbenzoyl)oxy)-2-hydroxybenzoic acid (11b)



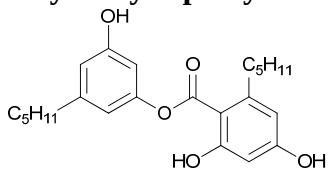
Following the procedure for anziaic acid: Compound **10b** (97 mg, 0.15 mmol), 10 wt% Pd/C (32 mg, 33 wt%), ethyl acetate (5 mL); Product: solid (55 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.95 (d, J = 8.4 Hz, 1 H), 6.78-6.75 (m, 2 H), 6.29 (d, J = 2.4 Hz, 1 H), 6.23 (d, J = 2.4 Hz, 1 H), 2.88 (t, J = 7.6 Hz, 2 H), 1.65-1.64 (m, 2 H), 1.34-1.32 (m, 4 H), 0.87 (t, J = 6.8 Hz 3 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 171.61, 168.87, 164.42, 163.06, 162.96, 155.65, 147.84, 131.46, 112.68, 110.77, 110.74, 109.94, 104.09, 100.59, 36.15, 31.74, 31.63, 22.17, 12.97; MS (ESI^-): m/z 359.1 $[M-H]^-$; HRMS (ESI^+) Calcd for $C_{19}H_{20}O_7$ ($M+H^+$): 361.1282, Found: 361.1280; HPLC purity: 98.0% (254 nm), t_R: 6.91 min; 98.3% (220 nm), t_R: 6.91 min.

4-((2,4-dihydroxybenzoyl)oxy)-2-hydroxybenzoic acid (11c)



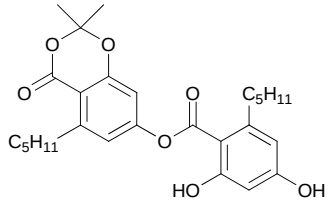
Following the procedure for anziaic acid: Compound **10c** (54 mg, 0.1 mmol), 10 wt% Pd/C (20 mg, 37 wt%), ethyl acetate (4 mL); Product: solid (27.9 mg, 99%). ^{1}H NMR (400 MHz, CD_3OD, ppm) δ 7.92 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 6.81 (d, *J* = 2.4 Hz, 1 H), 6.77 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.43 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.35 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100.5 MHz, CD_3OD, ppm) δ 171.62, 167.76, 165.33, 164.31, 162.99, 155.80, 131.96, 131.37, 112.72, 110.03, 108.35, 103.28, 102.31; MS (ESI^-): m/z 289.1 $[M-H]^-$; HRMS (ESI^+) Calcd for $C_{14}H_{10}O_7$ ($M+H^+$): 291.0500, Found: 291.0503; HPLC purity: 100% (254 nm), t_R: 6.29 min; 100% (220 nm), t_R: 6.29 min.

3-hydroxy-5-pentylphenyl 2,4-dihydroxy-6-pentylbenzoate (11d)



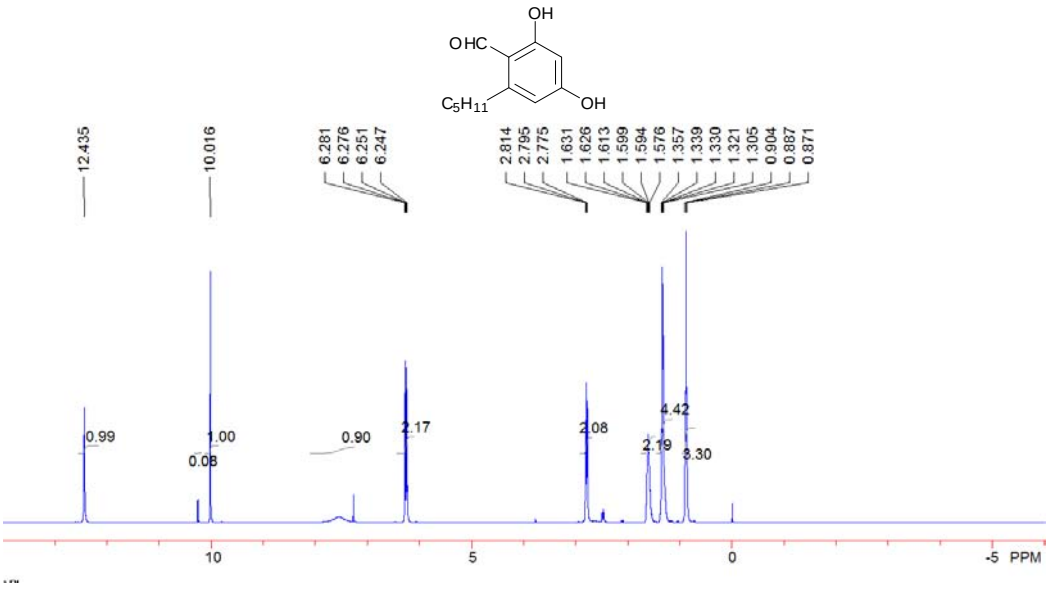
Following the procedure for anziaic acid: Compound **10d** (60 mg, 0.105 mmol), 10 wt% Pd/C (21 mg, 35 wt%), ethyl acetate (4 mL); Product: solid (33 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.50 (br, 1 H), 6.59 (s, 1 H), 6.56 (s, 1 H), 6.49 (s, 1 H), 6. 30 (s, 2 H) 5.94 (br, 2 H), 2.93 (t, *J* = 7.2 Hz, 2 H), 2.55 (t, *J* = 7.6 Hz, 2 H), 1.63-1.58 (m, 4 H), 1.31-1.30 (m, 8 H), 0.90-0.83 (m, 6 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 170.45, 165.75, 161.31, 156.37, 150.51, 149.55, 146.24, 113.83, 113.70, 111.55, 106.59, 104.23, 101.60, 37.11, 35.74, 32.00, 31.84, 31.43, 30.60, 22.56, 22.48, 14.01, 13.98; MS (ESI^-): m/z 385.3 $[M-H]^-$; HRMS (ESI^+) Calcd for $C_{23}H_{30}O_5$ ($M+H^+$): 387.2166, Found: 387.2182; HPLC purity: 98.9% (254 nm), t_R: 7.69 min; 98.5% (220 nm), t_R: 7.69 min.

2,2-dimethyl-4-oxo-5-pentyl-4H-benzo[d][1,3]dioxin-7-yl 2,4-dihydroxy-6-pentyl benzoate (14)

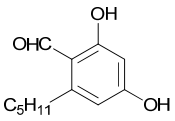


Following the procedure for anziaic acid: Compound **13** (80 mg, 0.12 mmol), 10 wt% Pd/C (26 mg, 33 wt%), ethyl acetate (4.5 mL); Eluent: hexane : ethyl acetate = 90 : 10; Product: solid (48 mg, 83%).^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.22 (s, 1 H), 6.77 (d, *J* = 1.6 Hz, 1 H), 6.71 (d, *J* = 2.0 Hz, 1 H), 6.35 (s, 1 H), 6.34 (s, 1 H), 5.94 (br, 1 H), 3.12 (t, *J* = 7.2 Hz, 2 H), 2.95 (t, *J* = 7.6 Hz, 2 H), 1.74 (s, 6 H), 1.67-1.63 (m, 4 H), 1.37-1.33 (m, 8 H) 0.91-0.87 (m, 6 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, ppm) δ 169.23, 166.39, 161.63, 159.77, 158.30, 154.69, 150.83, 149.33, 118.25, 111.58, 109.91, 108.62, 105.50, 103.78, 101.74, 37.19, 34.51, 32.01, 31.87, 31.80, 30.55, 25.68, 22.57, 22.48, 14.01; MS (ESI^-): m/z 468.9 $[M-H]^-$; HRMS (ESI^+) Calcd for $C_{27}H_{34}O_7$ ($M+Na^+$): 493.2197, Found: 493.2195; HPLC purity: 95.9% (254 nm), t_R: 8.11 min; 95.7% (220 nm), t_R: 8.11 min.

^{1}H NMR for compound 2



HPLC for compound 2



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==== Shimadzu LCsolution Analysis Report ====

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Batch File Name	:
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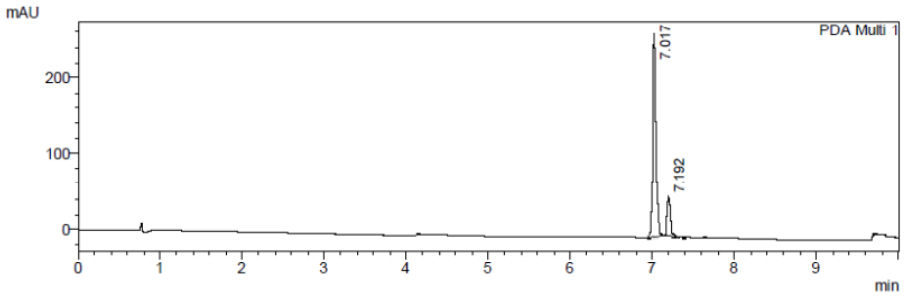

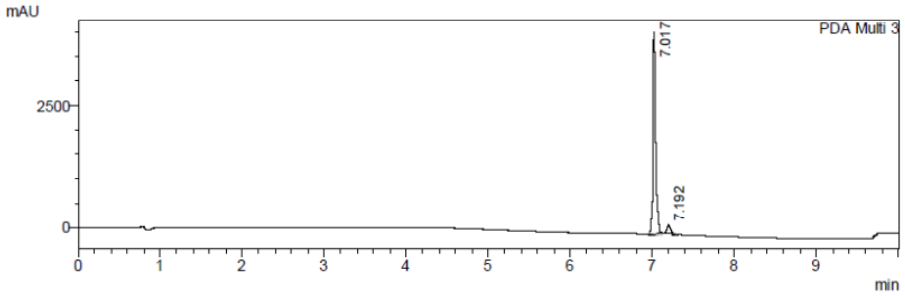

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PeakTable

PDA Ch3 220nm 4nm

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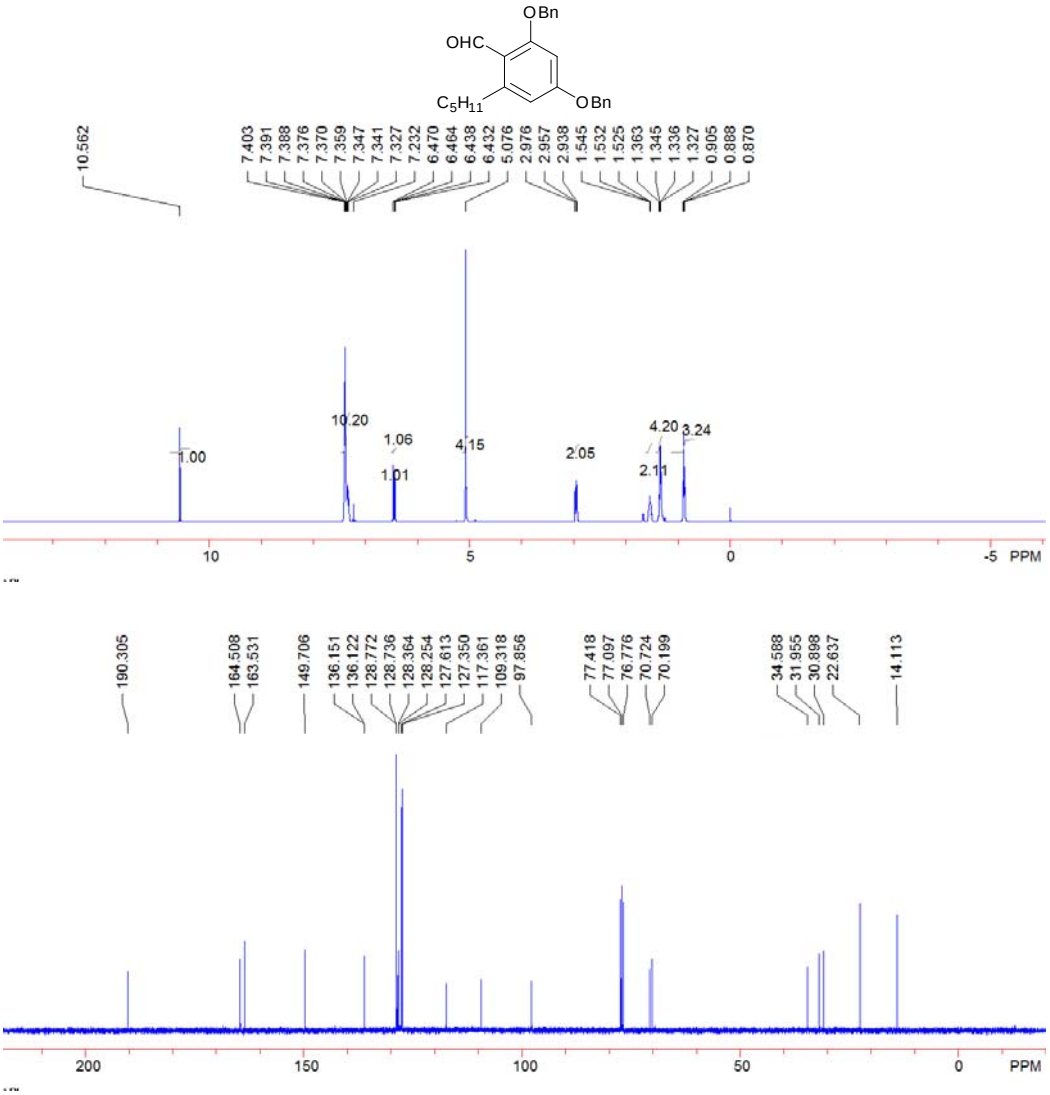
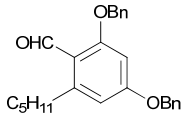
^{1}H and ^{13}C NMR for 2,4-bis(benzyloxy)-6-pentylbenzaldehyde



HPLC for 2,4-bis(benzyloxy)-6-pentylbenzaldehyde



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==== Shimadzu LCsolution Analysis Report ====

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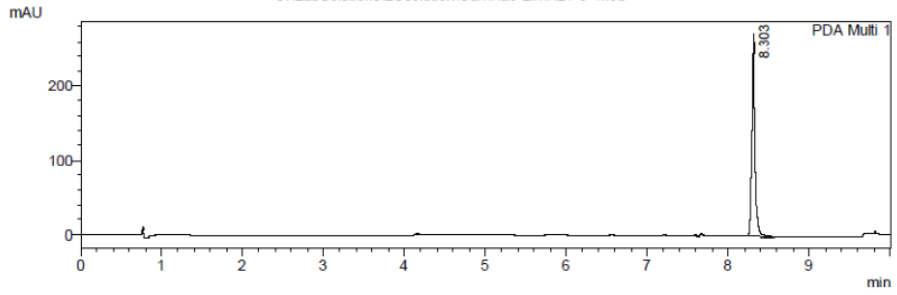

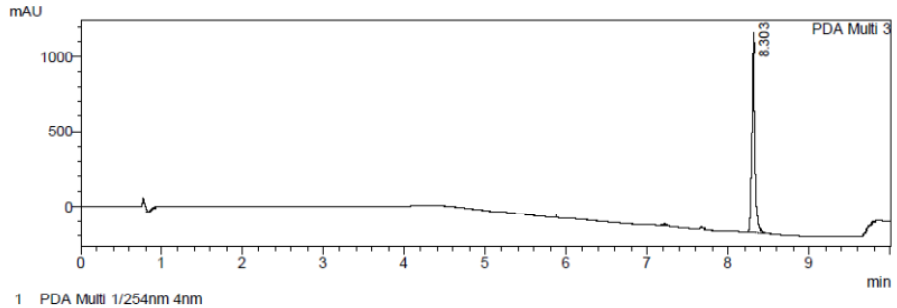

1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

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PeakTable

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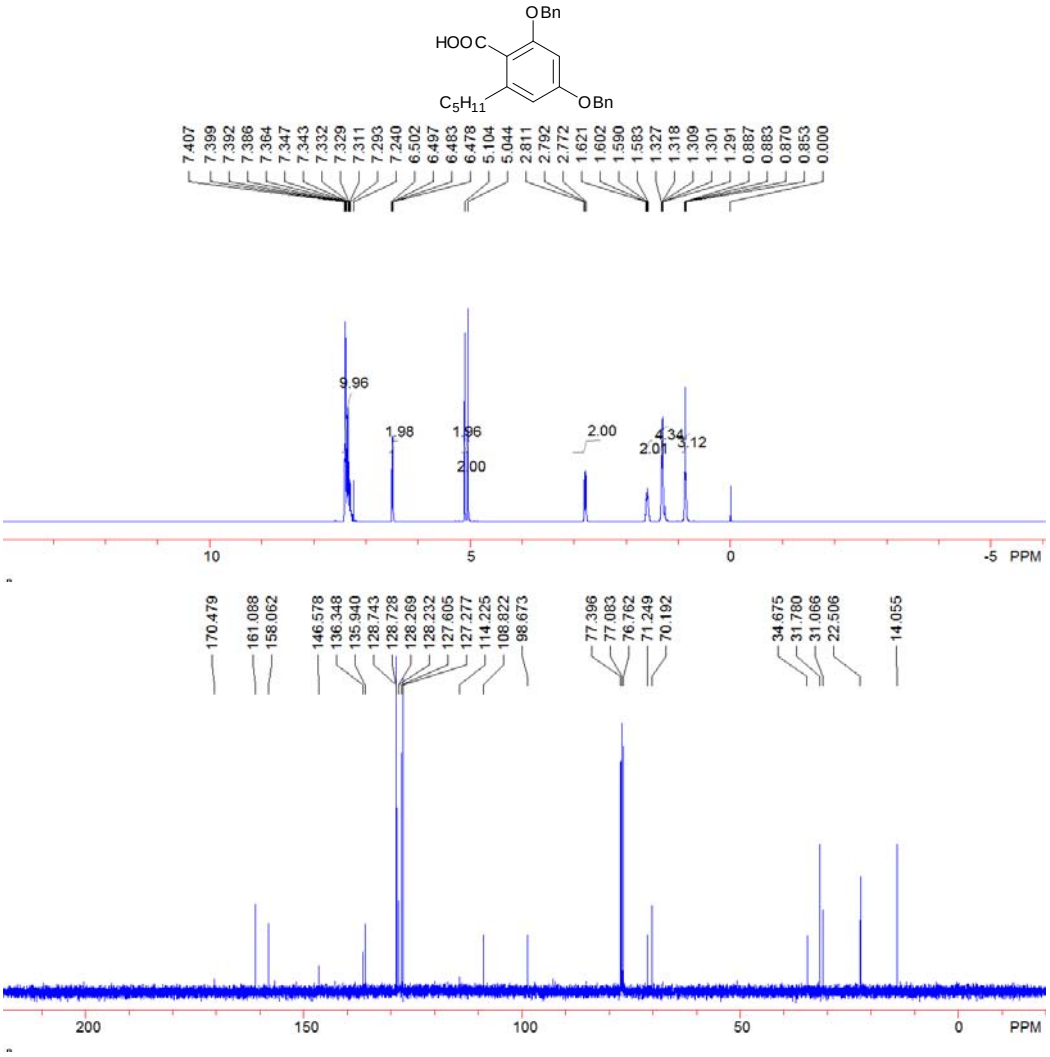
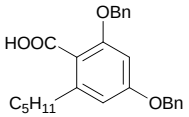
^{1}H and ^{13}C NMR for compound 3



HPLC for compound 3



11/12/2012 12:29:30 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-12-1.lcd

Sample Name	: HL1-12-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 15 uL
Data File Name	: HL1-12-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
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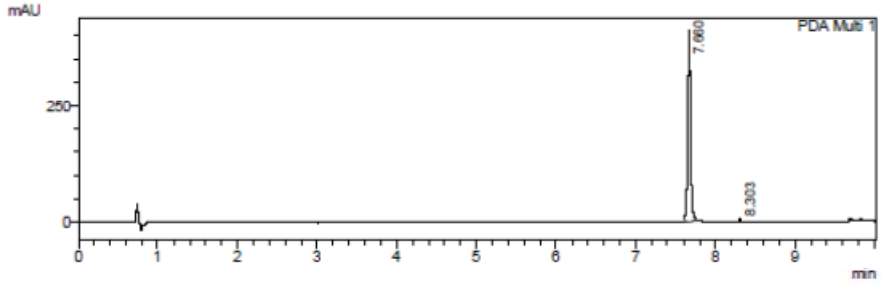
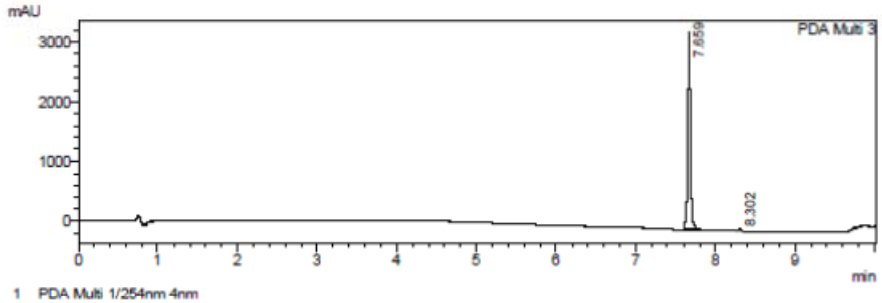




1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.660	1123058	411237	98.917	98.954
2	8.303	12301	4345	1.083	1.046
Total		1135359	415582	100.000	100.000

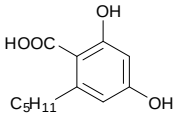
PeakTable

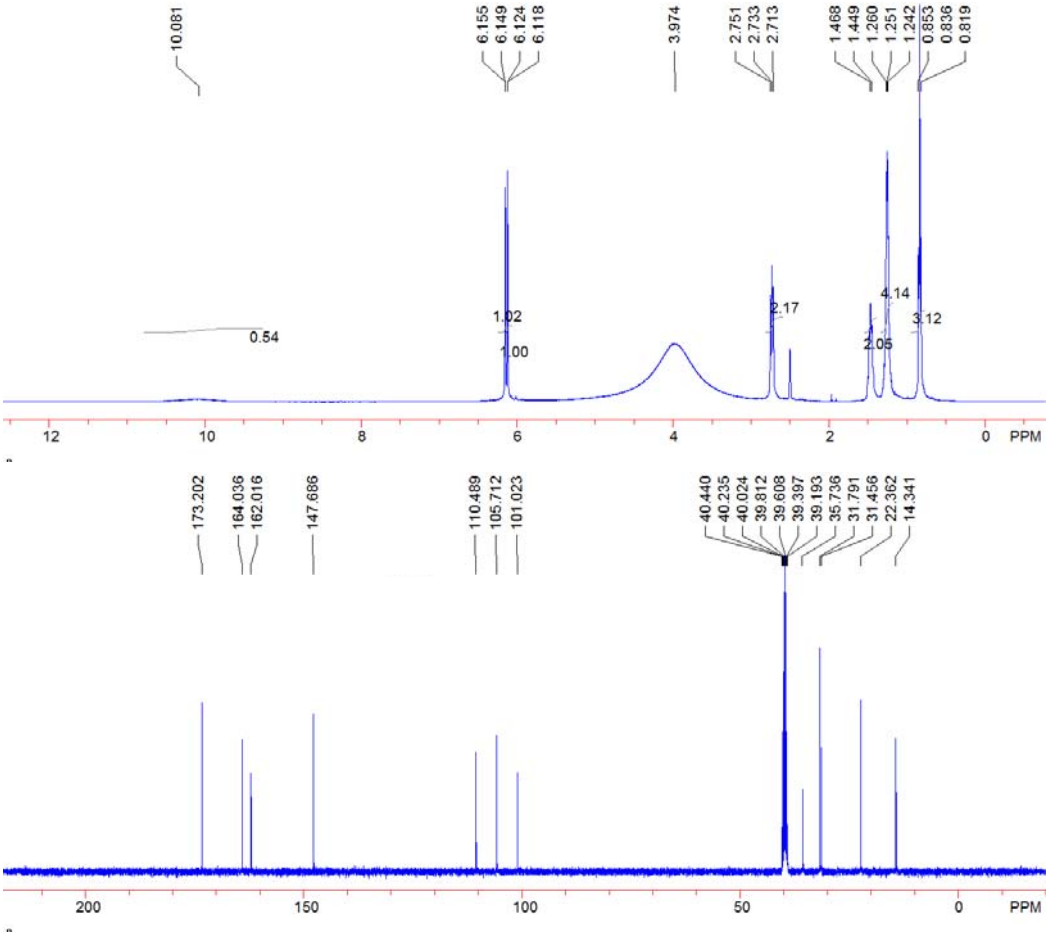
PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.659	8248983	3309535	99.299	99.384
2	8.302	58226	20527	0.701	0.616
Total		8307210	3330062	100.000	100.000

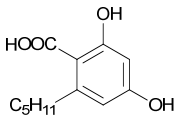
C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-12-1.lcd

^{1}H and ^{13}C NMR for compound 4





HPLC for compound 4



8/17/2013 10:48:17 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-15-1.lcd

Sample Name	: HL1-15-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: HL1-15-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 11/19/2012 3:23:06 PM

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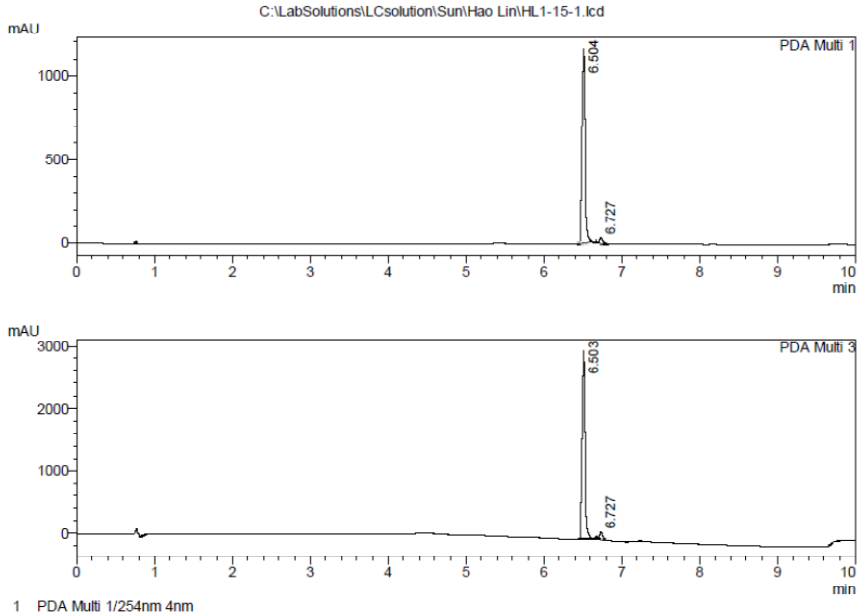

1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.504	3096627	1125054	96.475	97.299
2	6.727	113135	31231	3.525	2.701
Total		3209762	1156284	100.000	100.000

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.503	7422307	3019484	95.201	96.521
2	6.727	374143	108846	4.799	3.479
Total		7796450	3128330	100.000	100.000

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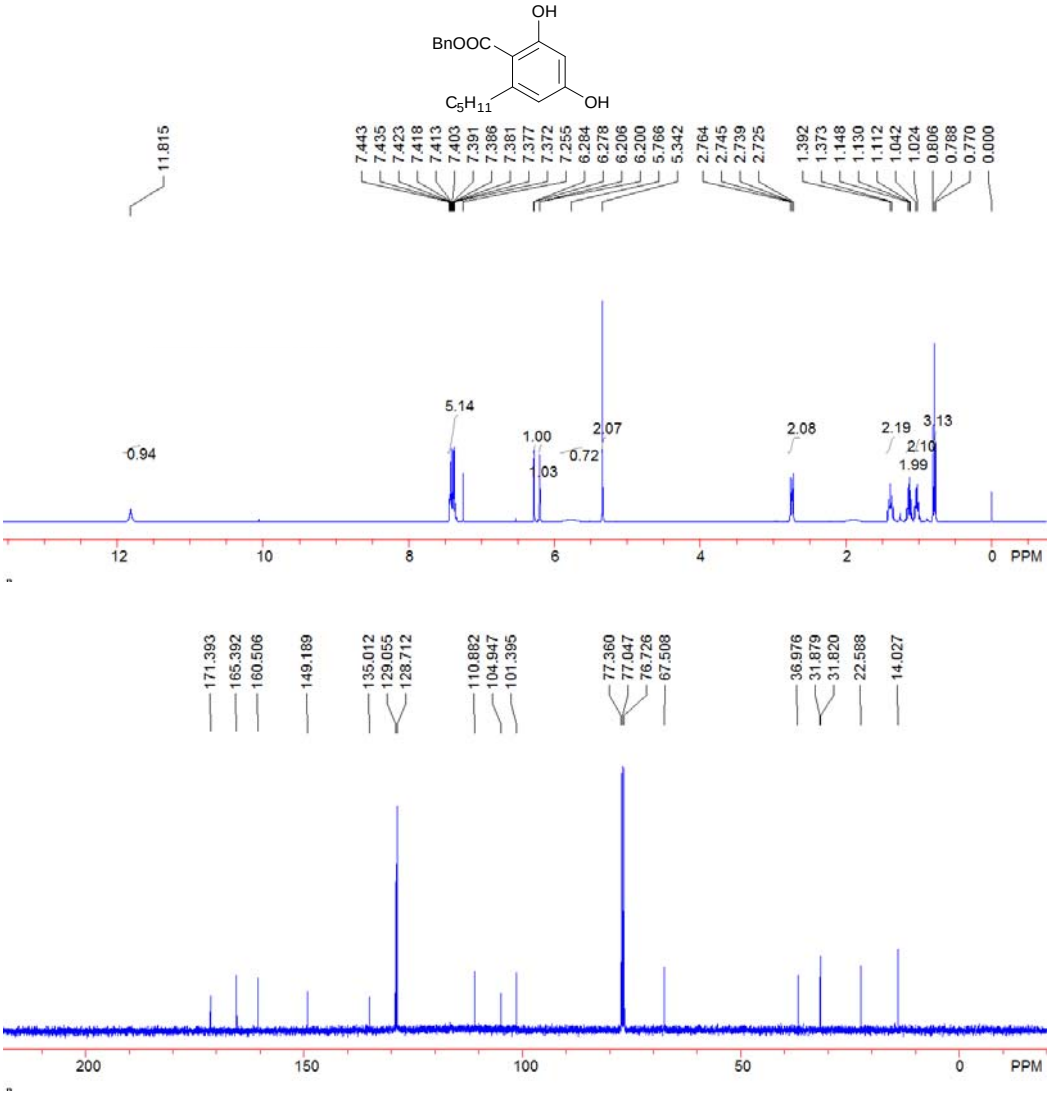
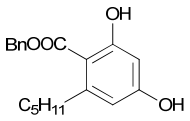
^{1}H and ^{13}C NMR for compound 5



HPLC for compound 5



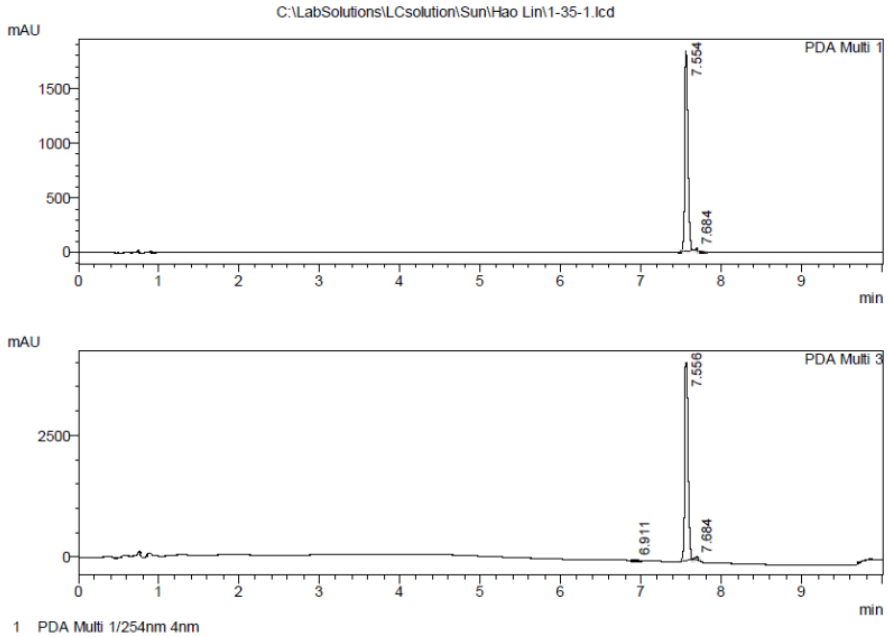
2/4/2013 16:28:09 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-35-1.lcd

Sample Name	: 1-35-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-35-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 2/4/2013 4:15:11 PM

<Chromatogram>



1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.554	4823473	1804098	99.668	98.978
2	7.684	16062	18633	0.332	1.022
Total		4839535	1822730	100.000	100.000

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.911	101670	38638	0.836	0.922
2	7.556	11888215	4069080	97.706	97.110
3	7.684	177477	82470	1.459	1.968
Total		12167363	4190187	100.000	100.000

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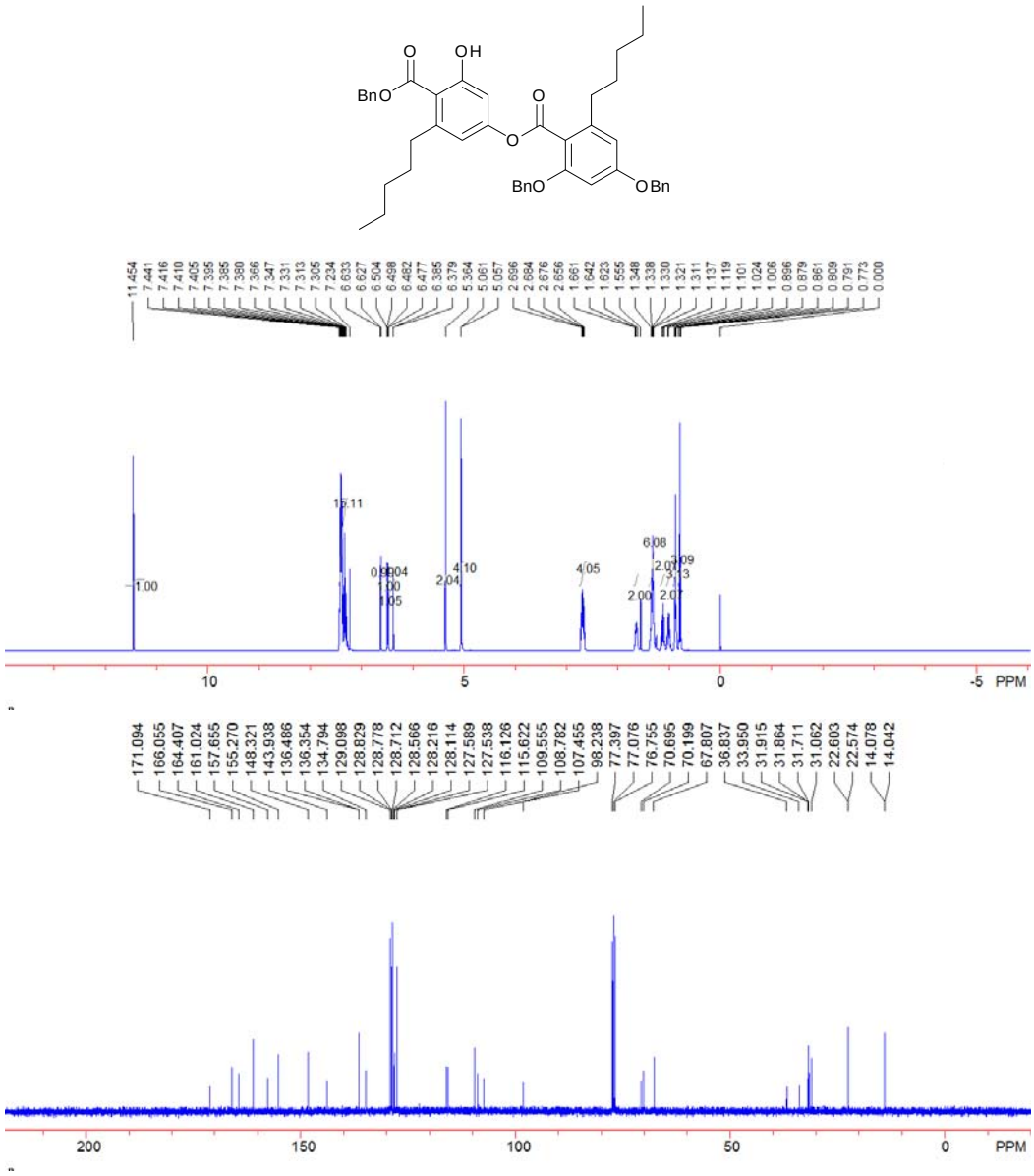
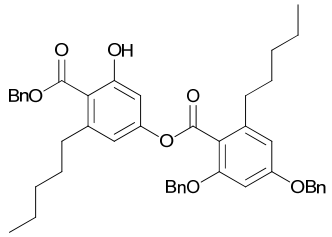
^{1}H and ^{13}C NMR for compound 6



HPLC for compound 6



11/27/2012 12:22:57 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-23-1.lcd

Sample Name	: HL1-23-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: HL1-23-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 11/27/2012 12:03:59 PM

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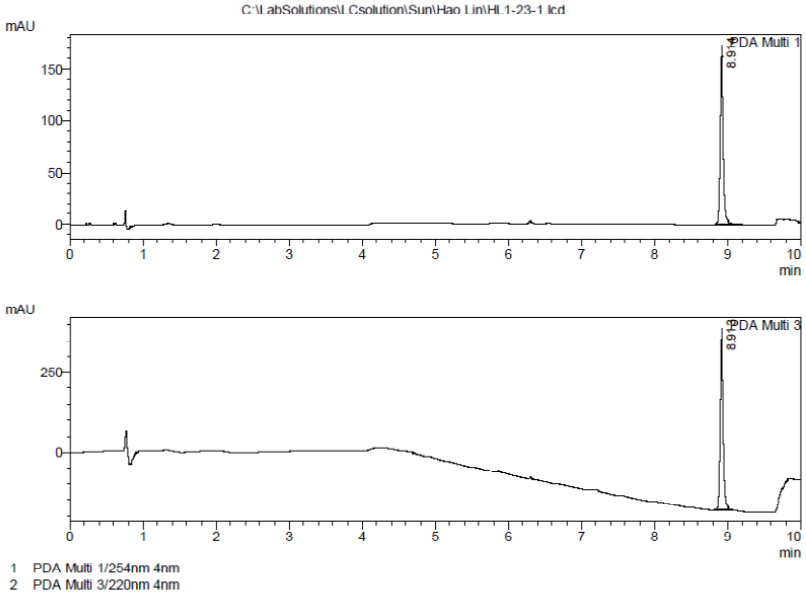

1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.914	499878	169449	100.000	100.000
Total		499878	169449	100.000	100.000

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.913	1624437	568714	100.000	100.000
Total		1624437	568714	100.000	100.000

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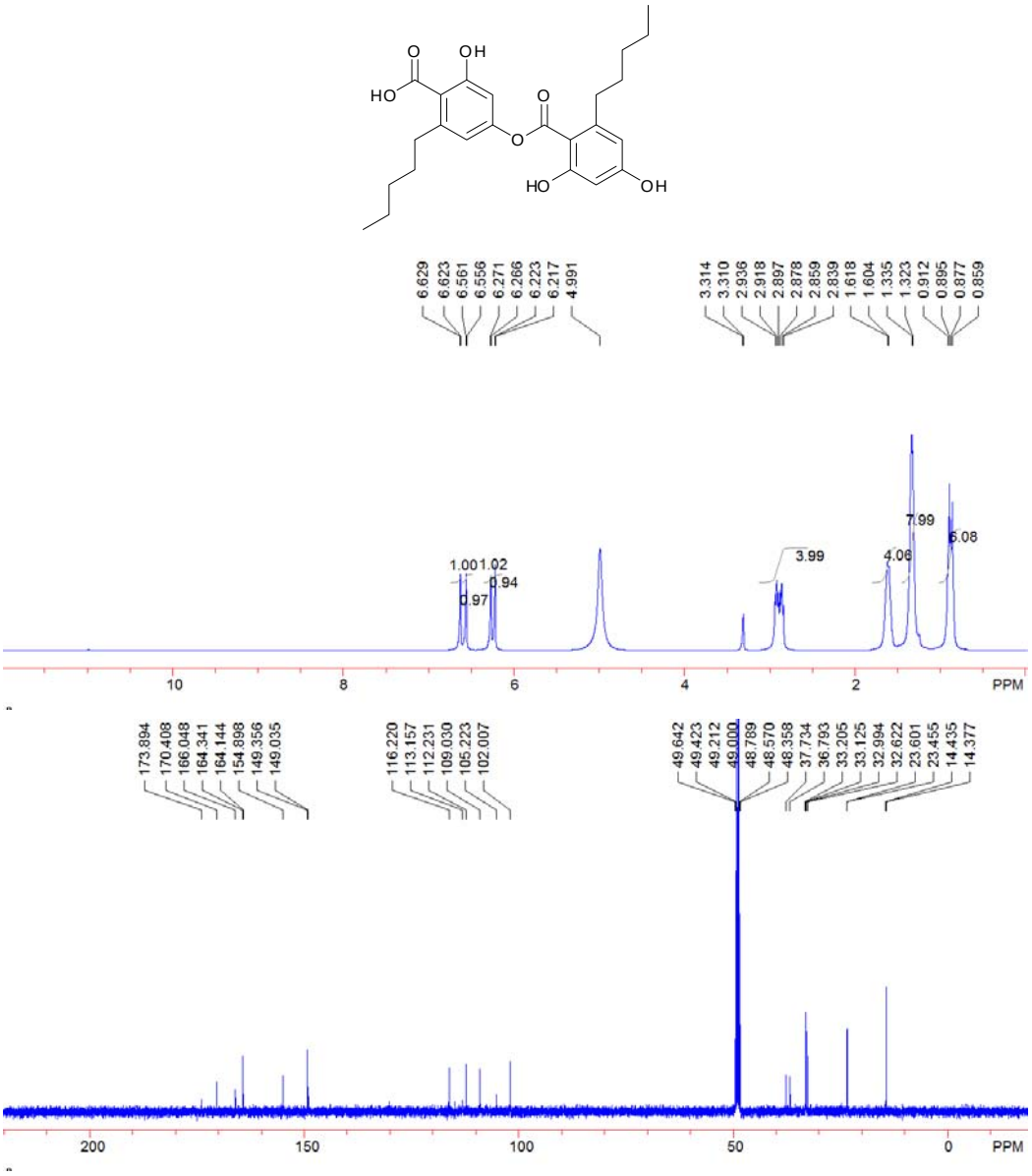
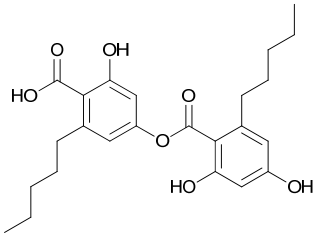
^{1}H and ^{13}C NMR for Anziaic acid



HPLC for Anziaic acid



5/7/2013 13:21:21 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-117-1.lcd

Sample Name	: 1-117-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-117-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 5/7/2013 10:45:39 AM

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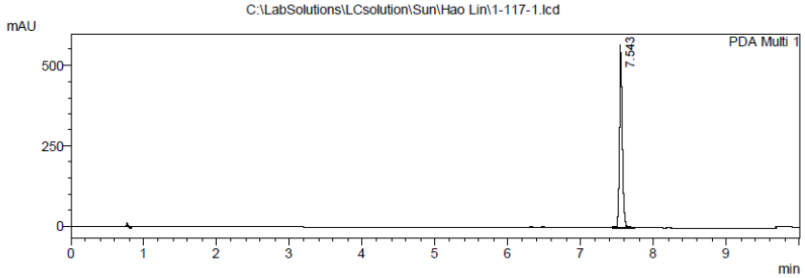
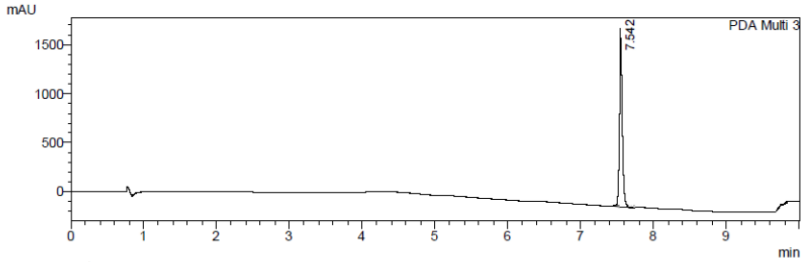




1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.543	1606982	555677	100.000	100.000
Total		1606982	555677	100.000	100.000

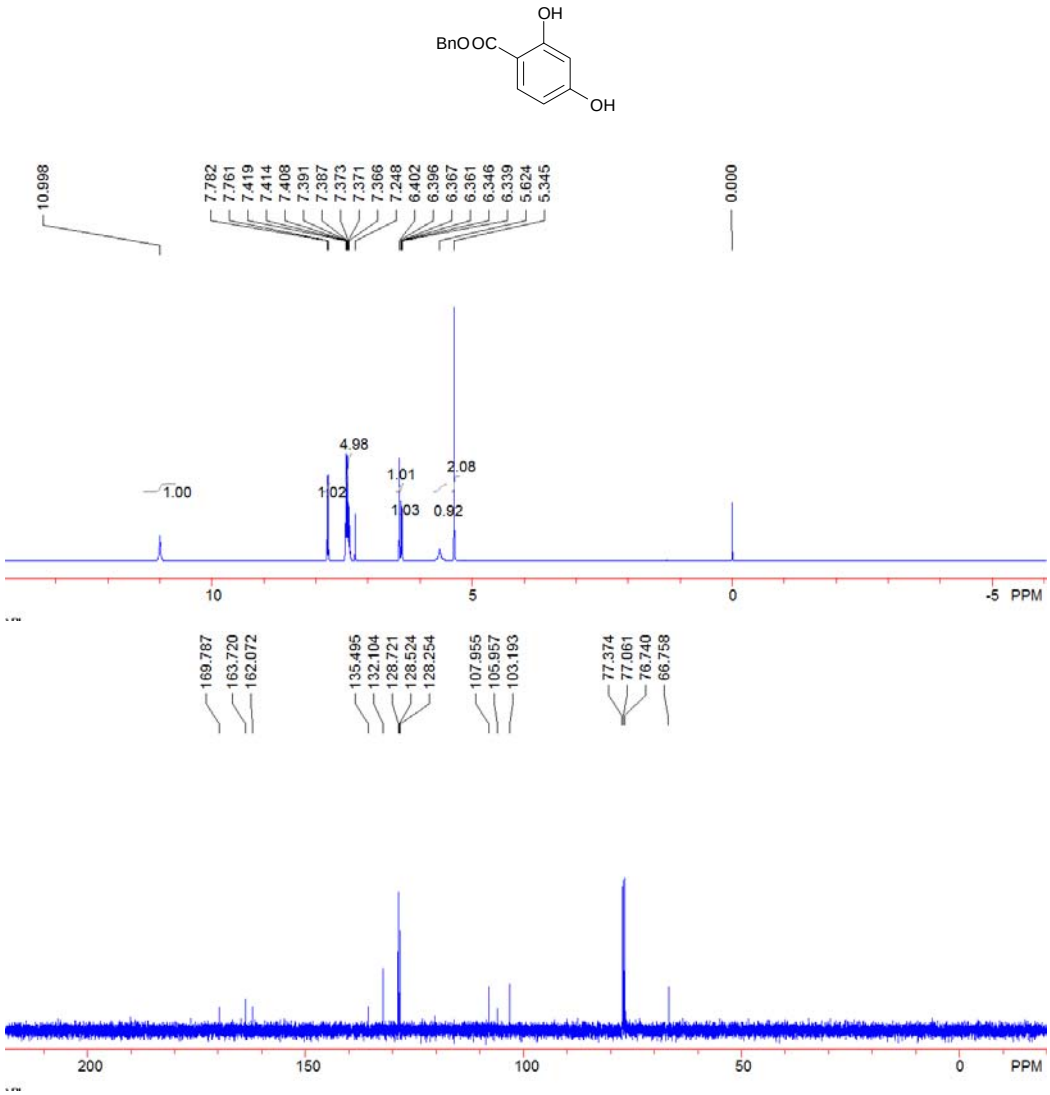
PeakTable

PDA Ch3 220nm 4nm

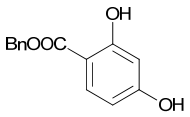
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.542	4966236	1815707	100.000	100.000
Total		4966236	1815707	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-117-1.lcd

^{1}H and ^{13}C NMR for compound 7



HPLC for compound 7



10/29/2012 15:42:36 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-3-1-1.lcd

Sample Name	: HL1-3-1-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: HL1-3-1-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 10/29/2012 2:15:43 PM

<Chromatogram>

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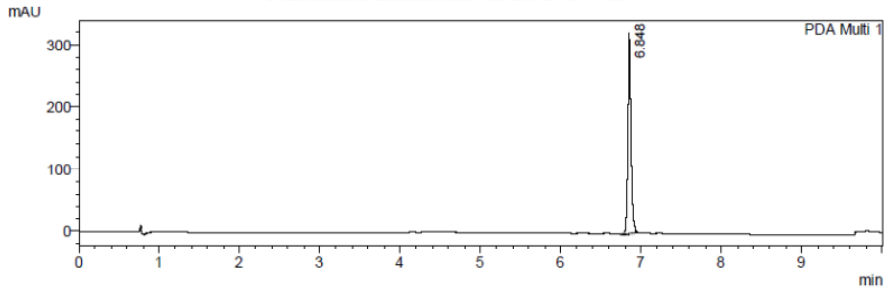
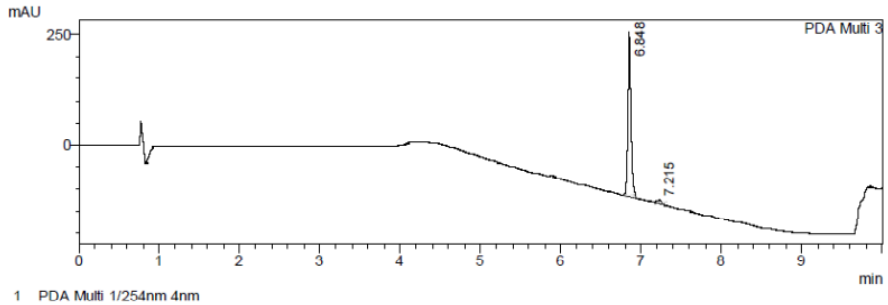




1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.848	901296	313878	100.000	100.000
Total		901296	313878	100.000	100.000

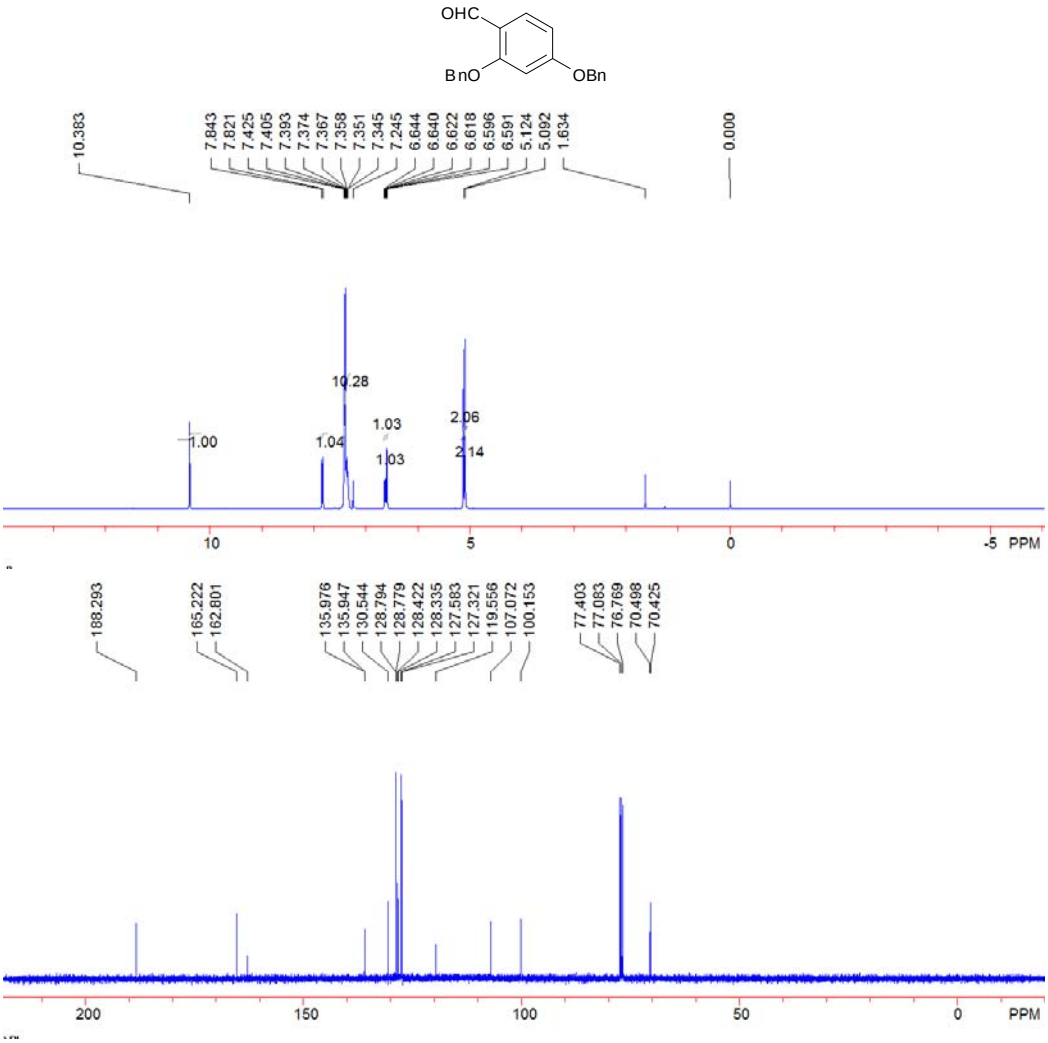
PeakTable

PDA Ch3 220nm 4nm

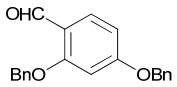
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.848	1033081	371322	97.088	97.654
2	7.215	30981	8922	2.912	2.346
Total		1064061	380243	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-3-1-1.lcd

^{1}H and ^{13}C NMR for 2,4-bis(benzyloxy)benzaldehyde



HPLC for 2,4-bis(benzyloxy)benzaldehyde



11/8/2012 12:03:28 1 / 1

==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: HL1-3-2-2
Tray#	: 1
Vail #	: 61
Injection Volume	: 15 uL
Data File Name	: HL1-3-2-2.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 11/8/2012 11:51:39 AM

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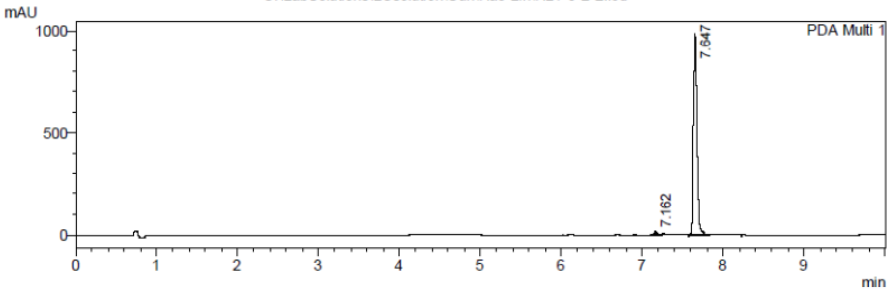

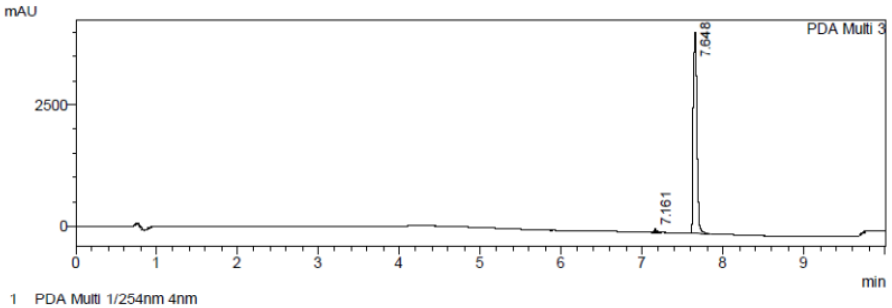

1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.162	37633	14314	1.333	1.460
2	7.647	2785244	966341	98.667	98.540
Total		2822877	980654	100.000	100.000

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.161	156121	59808	1.300	1.422
2	7.648	11855628	4144993	98.700	98.578
Total		12011750	4204801	100.000	100.000

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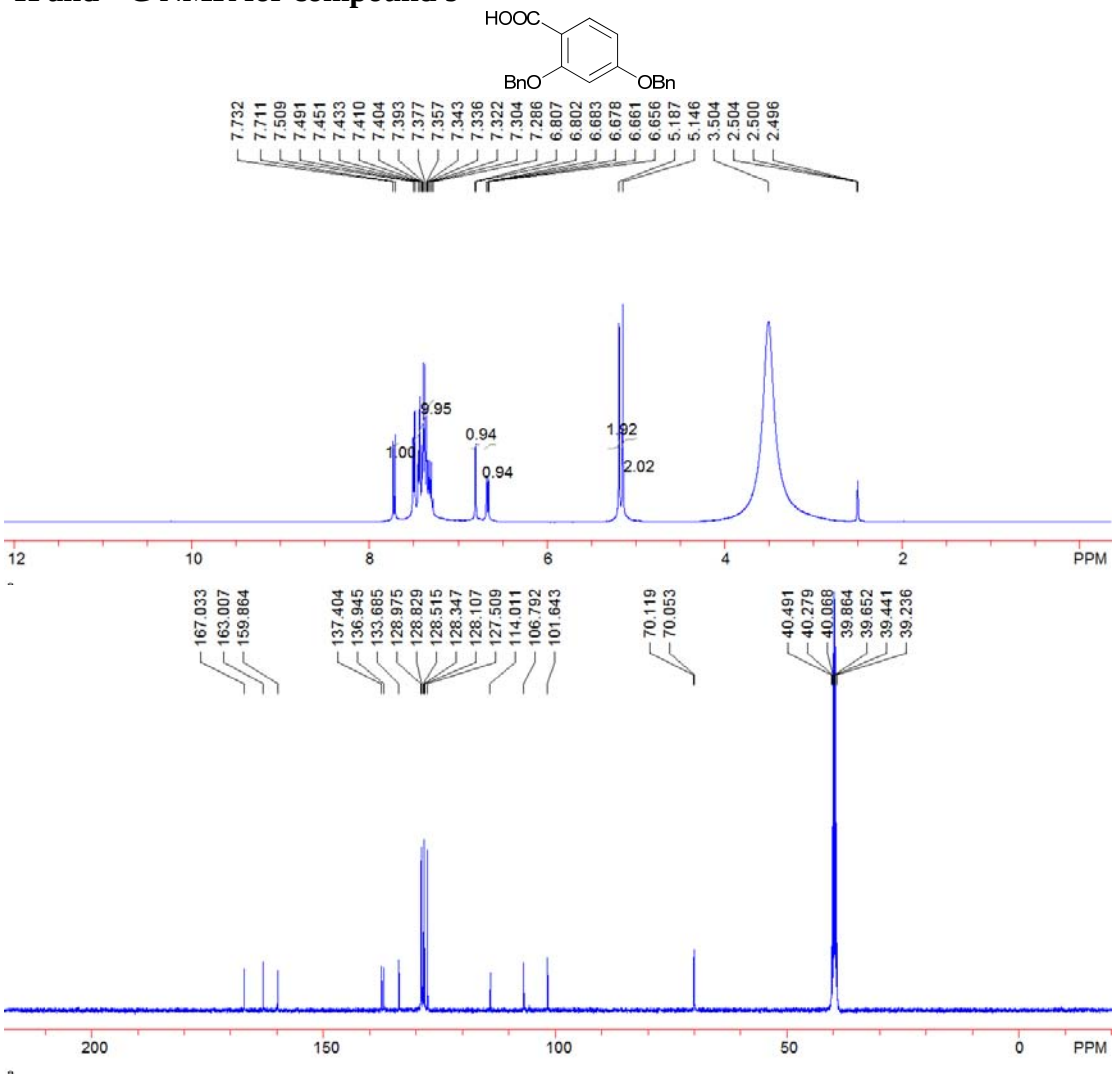
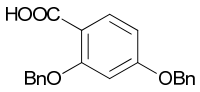
^{1}H and ^{13}C NMR for compound 9



HPLC for compound 9



5/10/2013 16:19:59 1 / 1

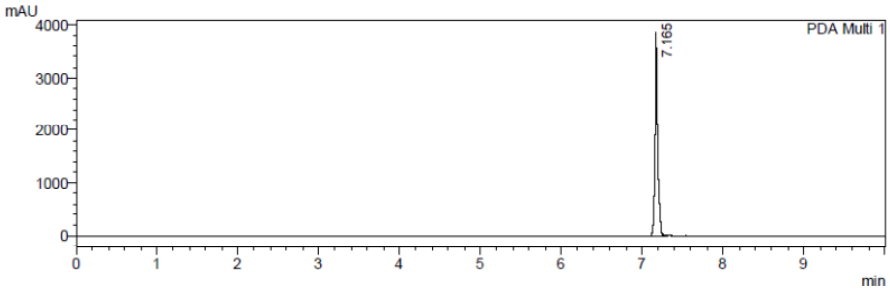
==== Shimadzu LCsolution Analysis Report ====

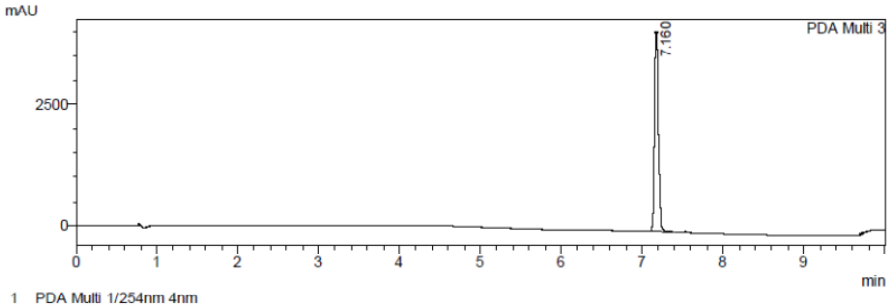
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-34-C.lcd

Sample Name	: 1-34-C
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-34-C.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 5/10/2013 4:07:25 PM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-34-C.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.165	10055200	3782986	100.000	100.000
Total		10055200	3782986	100.000	100.000

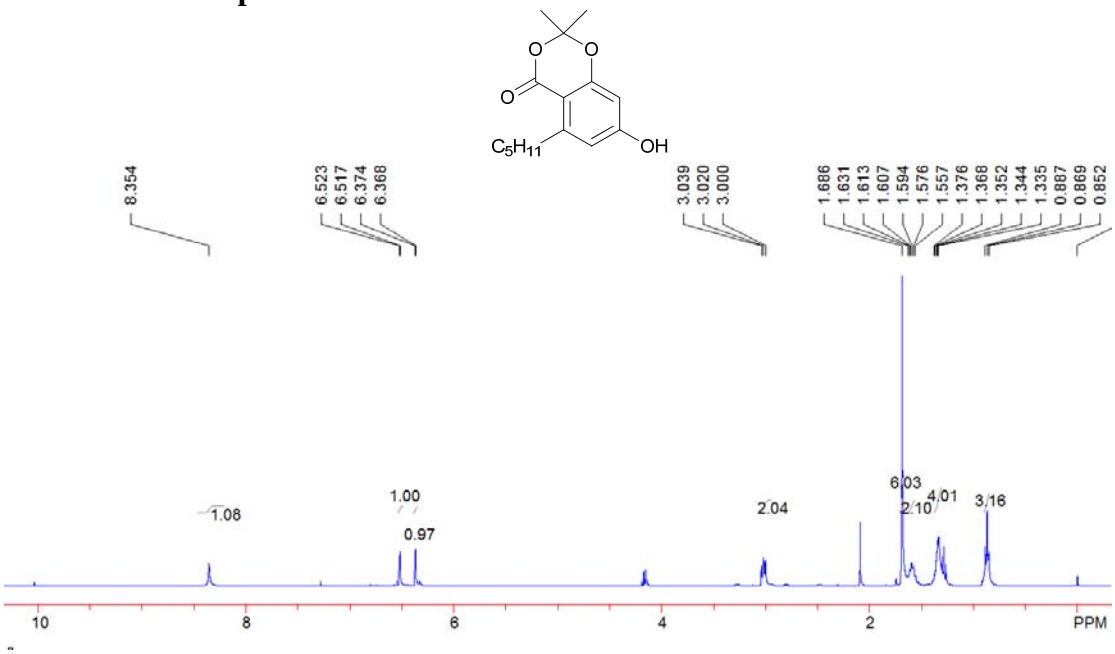
PeakTable

PDA Ch3 220nm 4nm

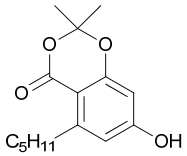
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.160	15533017	4119729	100.000	100.000
Total		15533017	4119729	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-34-C.lcd

^{1}H NMR for compound 12



HPLC for compound 12



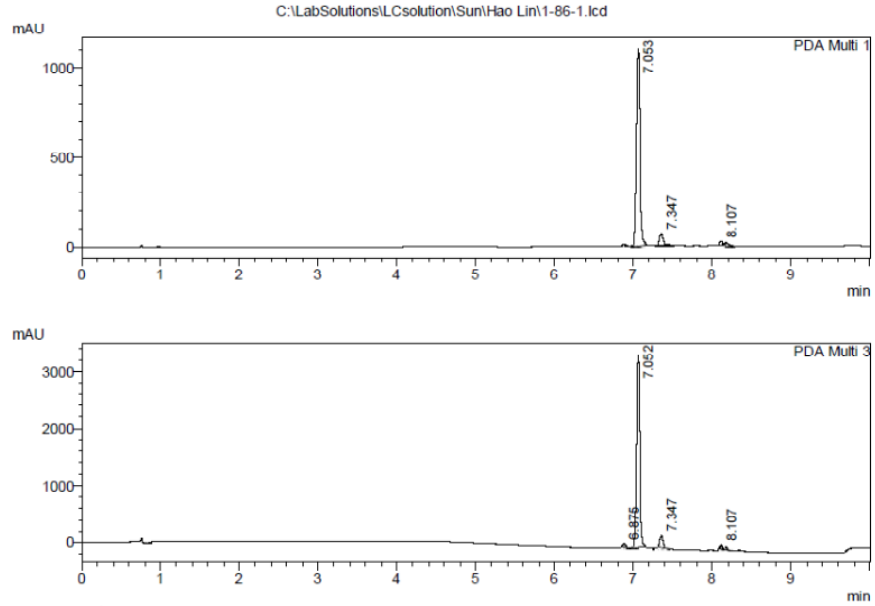
7/5/2013 11:59:08 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-86-1.lcd

Sample Name	: 1-86-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-86-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/10/2013 11:03:05 AM

<Chromatogram>



1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.053	3182446	1094335	89.660	91.819
2	7.347	230110	69433	6.483	5.826
3	8.107	136914	28073	3.857	2.355
Total		3549470	1191841	100.000	100.000

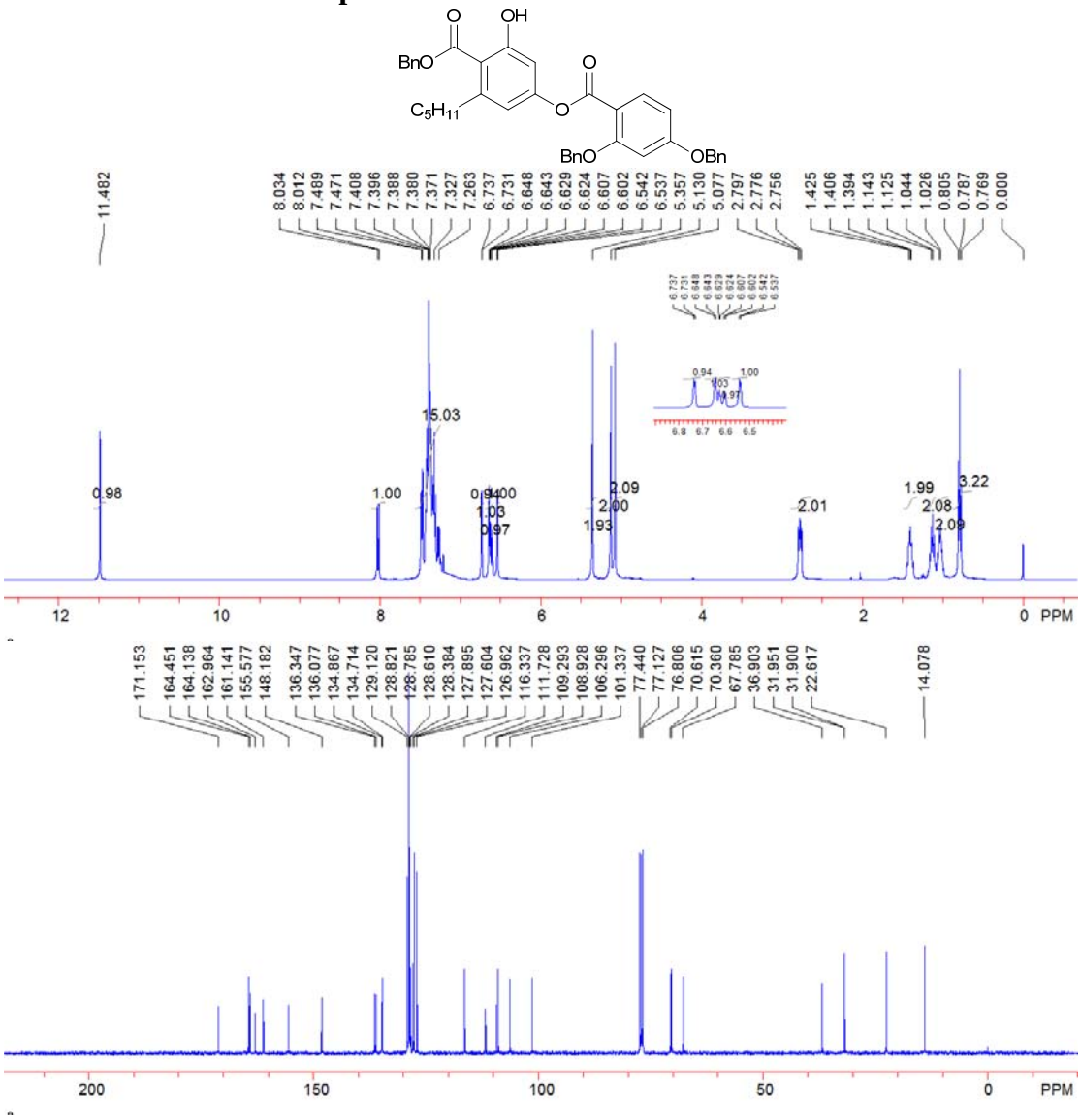
PeakTable

PDA Ch3 220nm 4nm

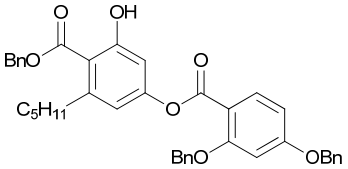
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.875	132626	68053	1.420	1.843
2	7.052	8423894	3357897	90.196	90.928
3	7.347	543212	206974	5.816	5.605
4	8.107	239794	60010	2.568	1.625
Total		9339526	3692933	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-86-1.lcd

^{1}H and ^{13}C NMR for compound 10a



HPLC for compound 10a



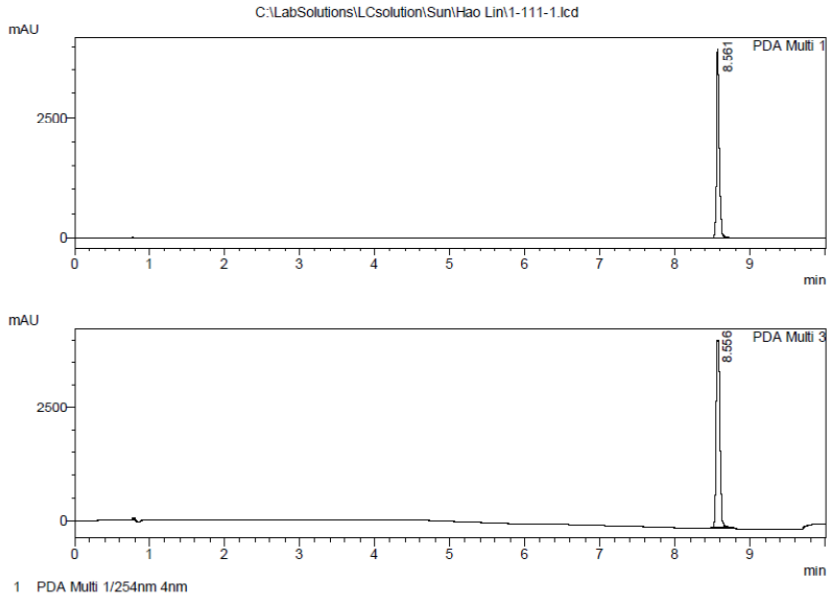
4/24/2013 15:21:25 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-111-1.lcd

Sample Name	: 1-111-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-111-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/24/2013 3:10:30 PM

<Chromatogram>



1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.561	9872927	3821836	100.000	100.000
Total		9872927	3821836	100.000	100.000

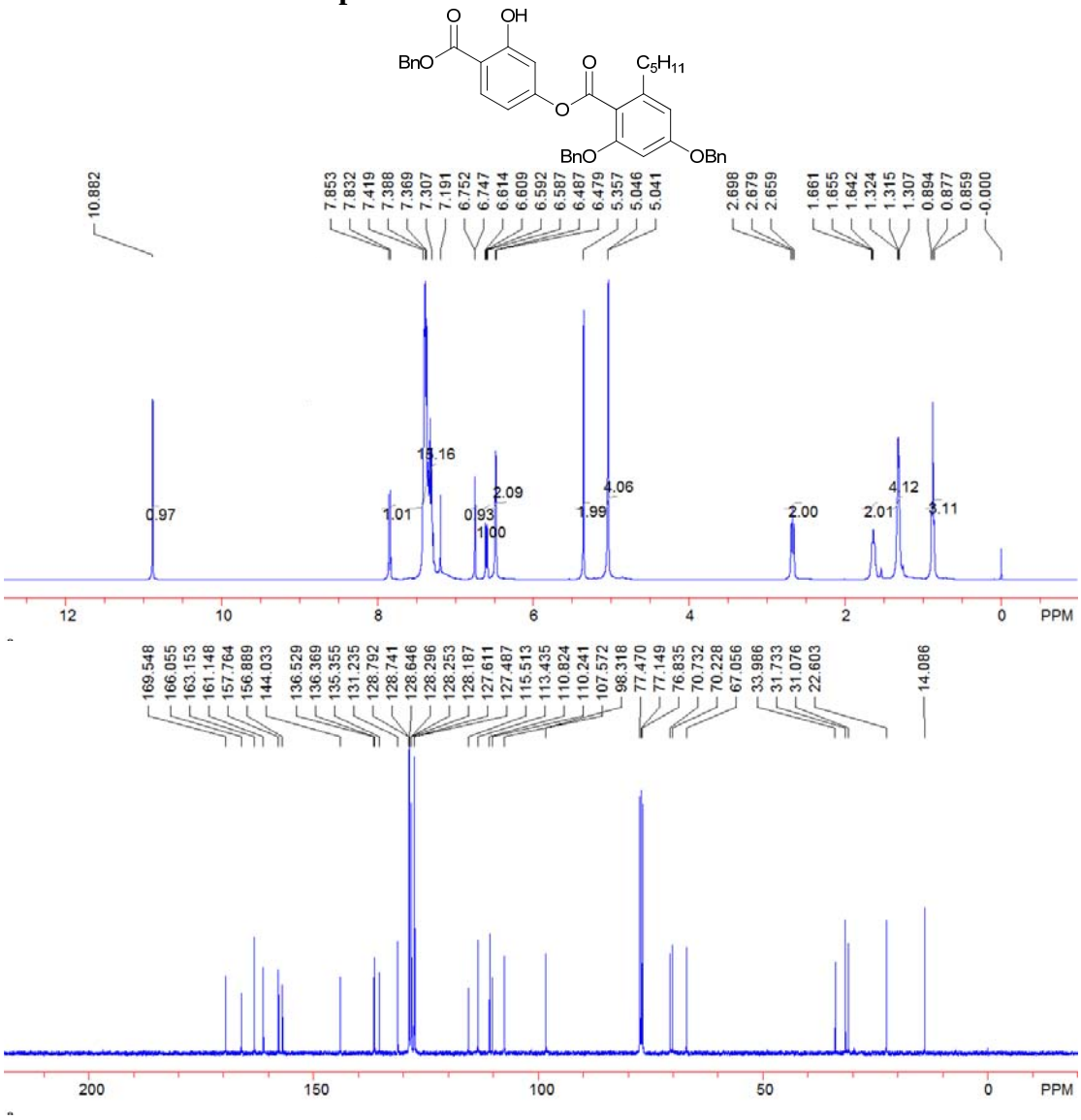
PeakTable

PDA Ch3 220nm 4nm

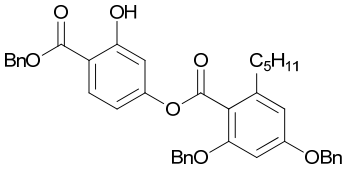
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.556	15323924	4161075	100.000	100.000
Total		15323924	4161075	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-111-1.lcd

^{1}H and ^{13}C NMR for compound 10b



HPLC for compound 10b



4/17/2013 14:47:38 1 / 1

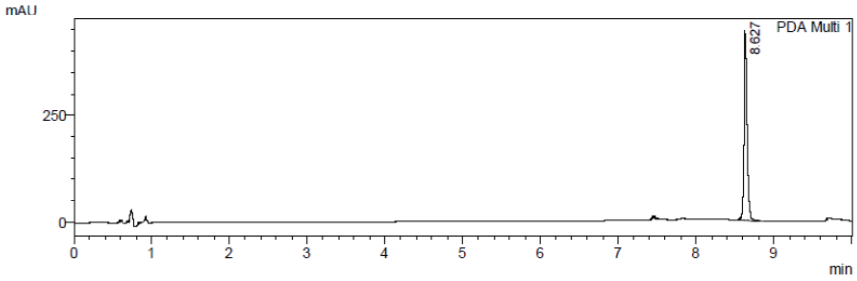
==== Shimadzu LCsolution Analysis Report ====

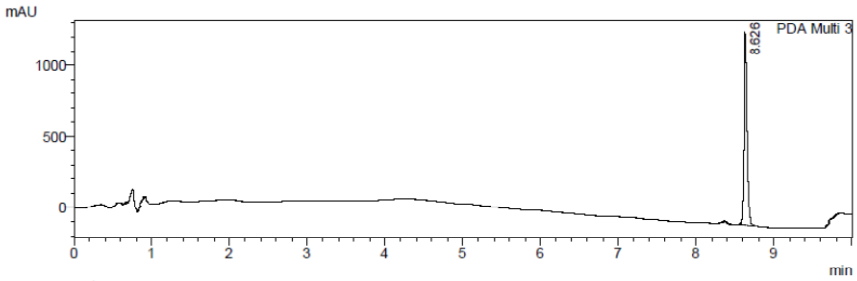
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-104-1.lcd

Sample Name	: 1-104-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 10 uL
Data File Name	: 1-104-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/17/2013 2:17:15 PM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-104-1.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.627	1235365	439541	100.000	100.000
Total		1235365	439541	100.000	100.000

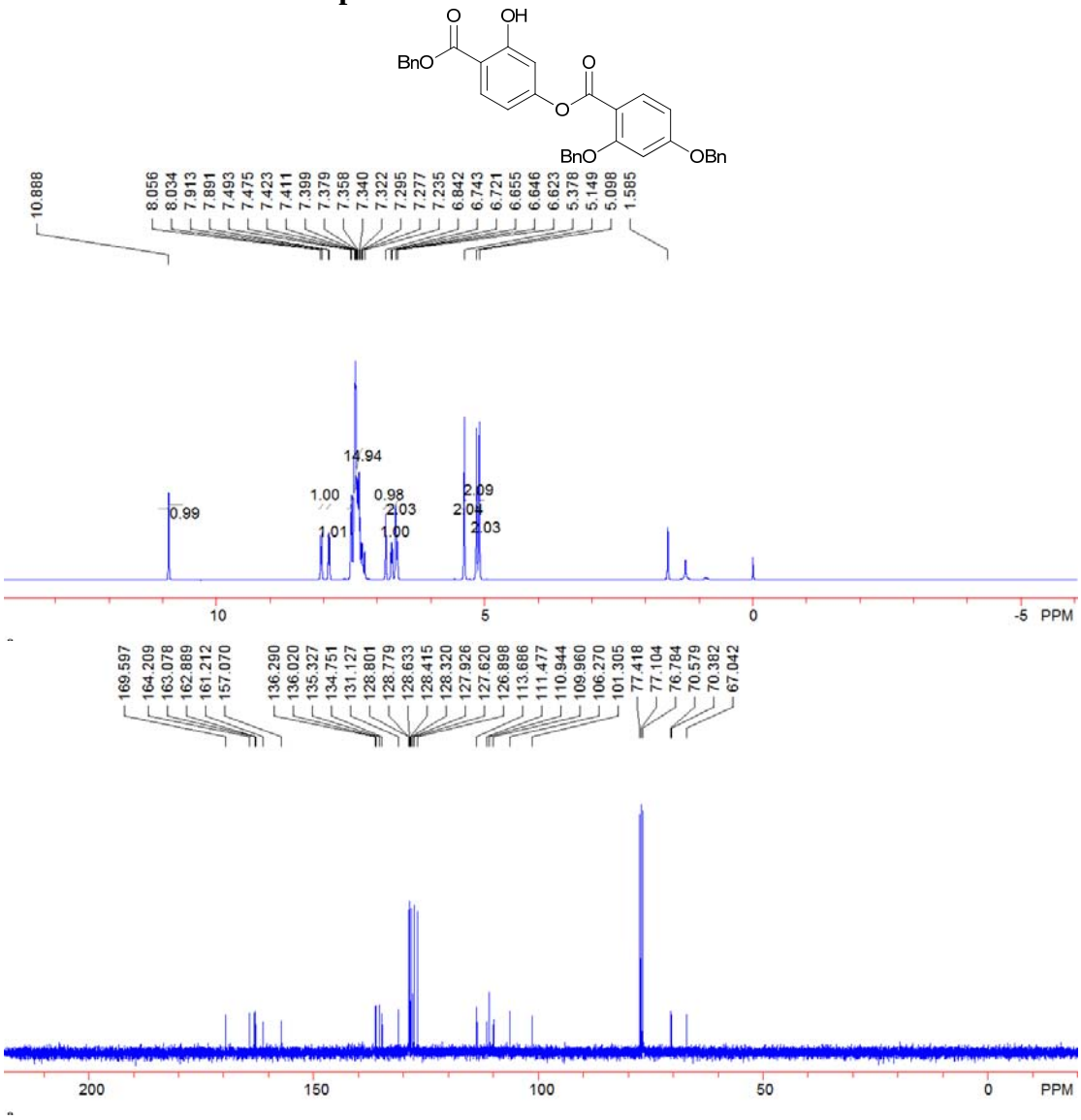
PeakTable

PDA Ch3 220nm 4nm

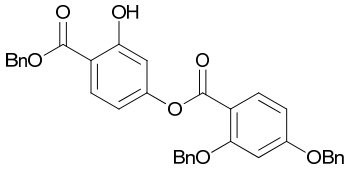
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.626	3693645	1359655	100.000	100.000
Total		3693645	1359655	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-104-1.lcd

^{1}H and ^{13}C NMR for compound 10c



HPLC for compound 10c



11/26/2012 10:27:27 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-20-1.lcd

Sample Name	: HL1-20-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 10 uL
Data File Name	: HL1-20-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 11/26/2012 10:03:10 AM

<Chromatogram>

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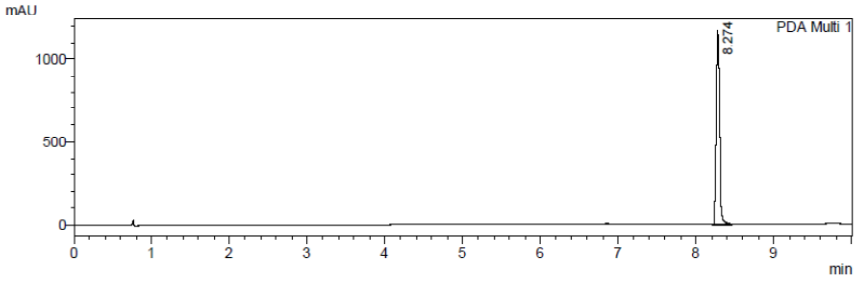
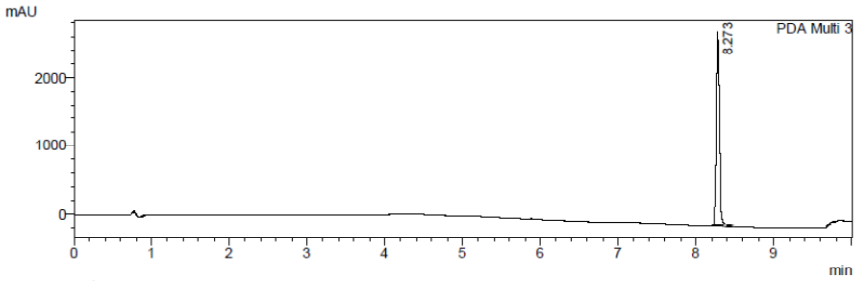




1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.274	3139171	1147617	100.000	100.000
Total		3139171	1147617	100.000	100.000

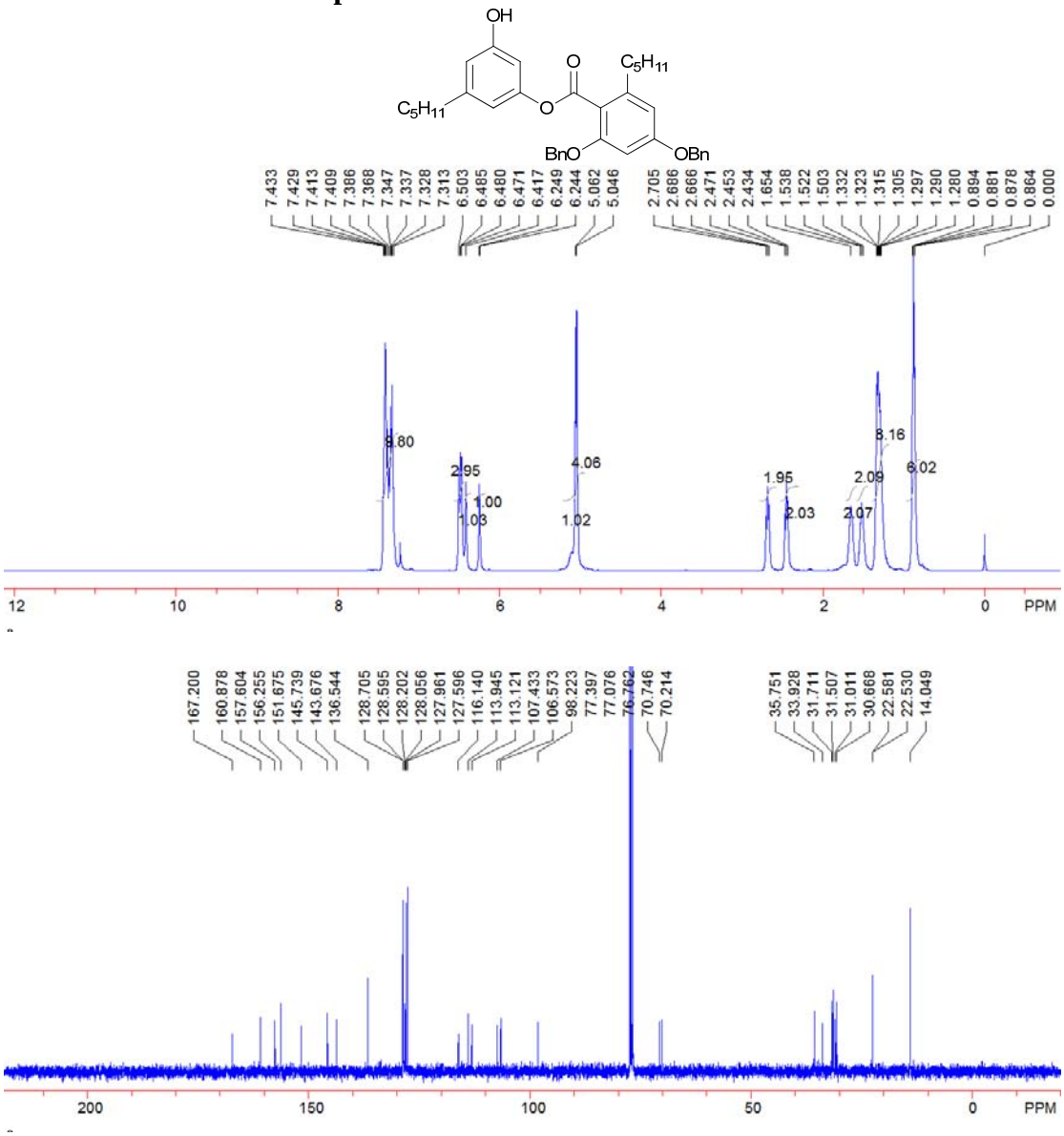
PeakTable

PDA Ch3 220nm 4nm

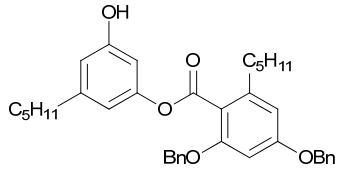
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.273	6747038	2837832	100.000	100.000
Total		6747038	2837832	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\HL1-20-1.lcd

^{1}H and ^{13}C NMR for compound 10d



HPLC for compound 10d



4/4/2013 10:04:52 1 / 1

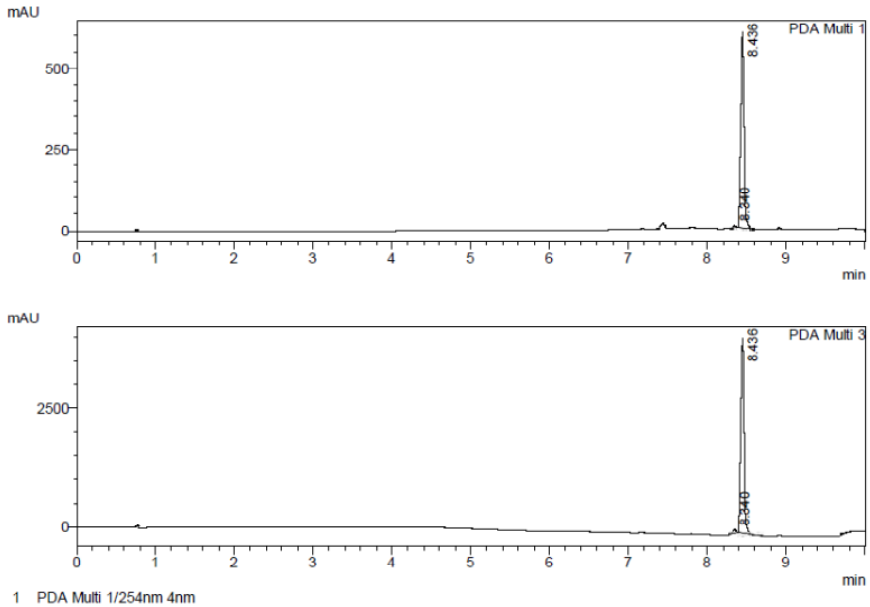
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-92-1.lcd

Sample Name	: 1-92-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-92-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/4/2013 9:38:02 AM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-92-1.lcd



1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.340	20052	8964	1.206	1.474
2	8.436	1642087	599356	98.794	98.526
Total		1662139	608320	100.000	100.000

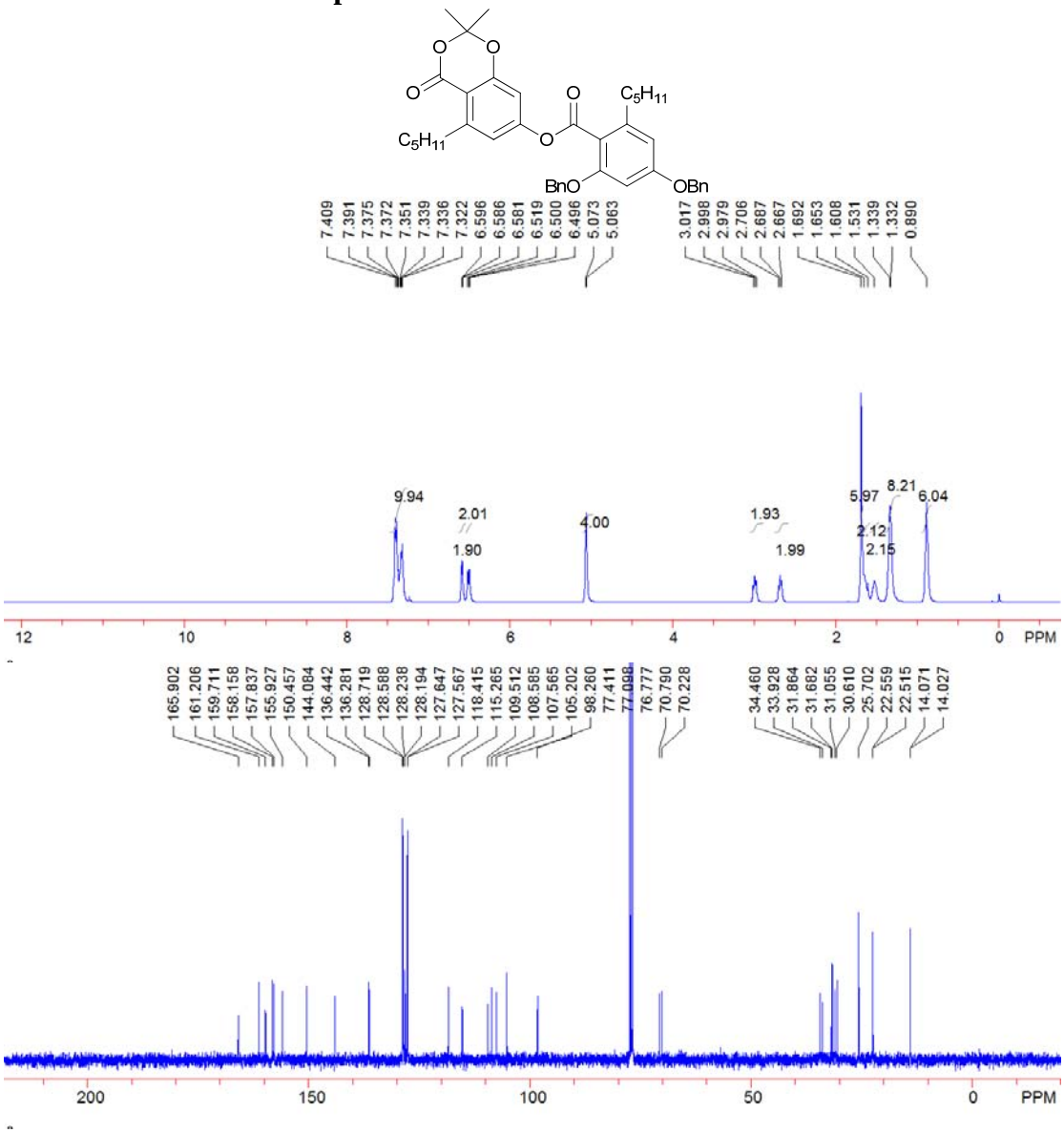
PeakTable

PDA Ch3 220nm 4nm

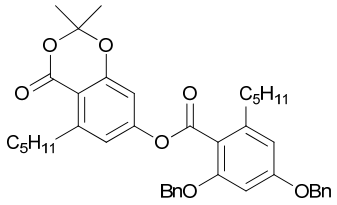
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.340	146226	66777	1.287	1.598
2	8.436	11219658	4110766	98.713	98.402
Total		11365885	4177543	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-92-1.lcd

^{1}H and ^{13}C NMR for compound 13



HPLC for compound 13



4/4/2013 11:27:01 1 / 1

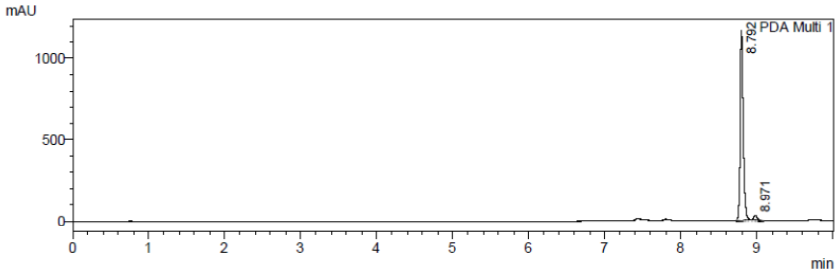
==== Shimadzu LCsolution Analysis Report ====

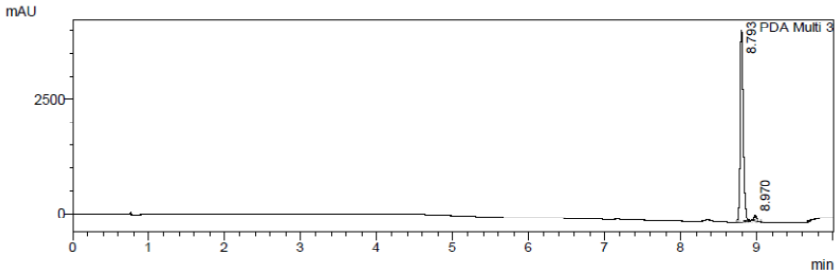
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-93-1.lcd

Sample Name	: 1-93-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-93-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/4/2013 10:03:48 AM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-93-1.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.792	3258076	1135672	97.738	97.681
2	8.971	75407	26959	2.262	2.319
Total		3333483	1162631	100.000	100.000

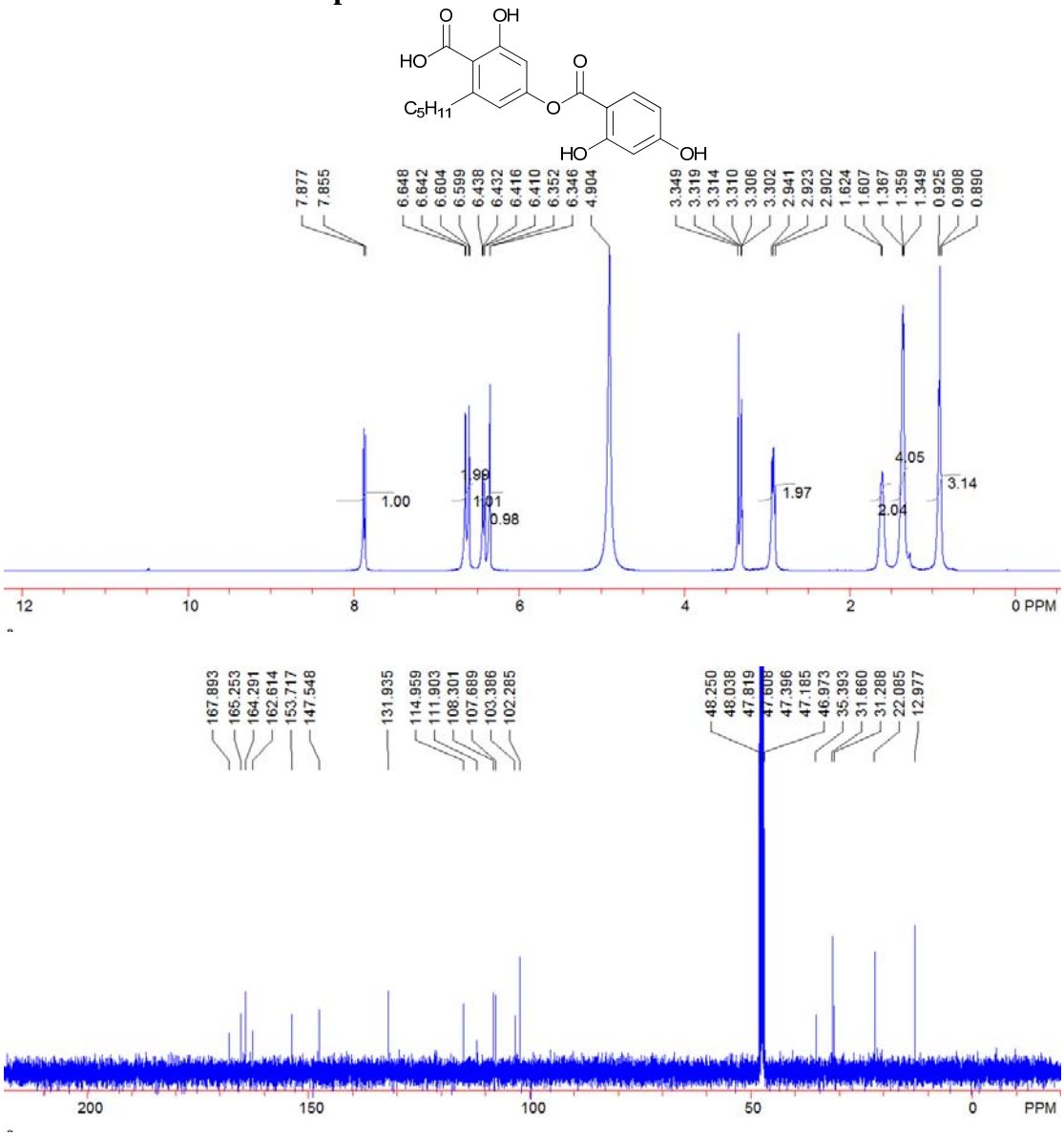
PeakTable

PDA Ch3 220nm 4nm

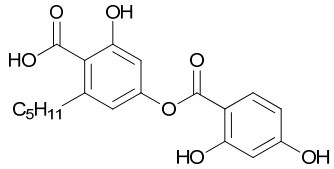
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.793	12190519	4166535	97.184	97.007
2	8.970	353282	128563	2.816	2.993
Total		12543801	4295098	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-93-1.lcd

^{1}H and ^{13}C NMR for compound 11a



HPLC for compound 11a



8/17/2013 11:21:41 1 / 1

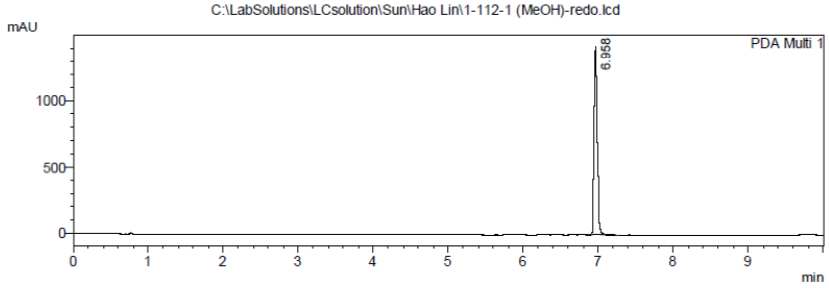
==== Shimadzu LCsolution Analysis Report ====

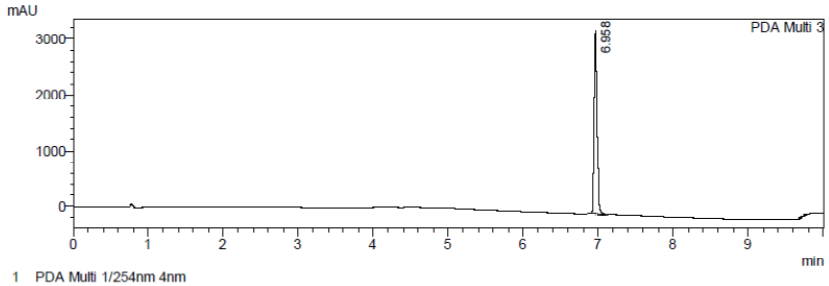
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-112-1 (MeOH)-redo.lcd

Sample Name	: 1-112-1 (MeOH)-redo
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-112-1 (MeOH)-redo.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 8/17/2013 11:03:58 AM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-112-1 (MeOH)-redo.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.958	3956350	1397126	100.000	100.000
Total		3956350	1397126	100.000	100.000

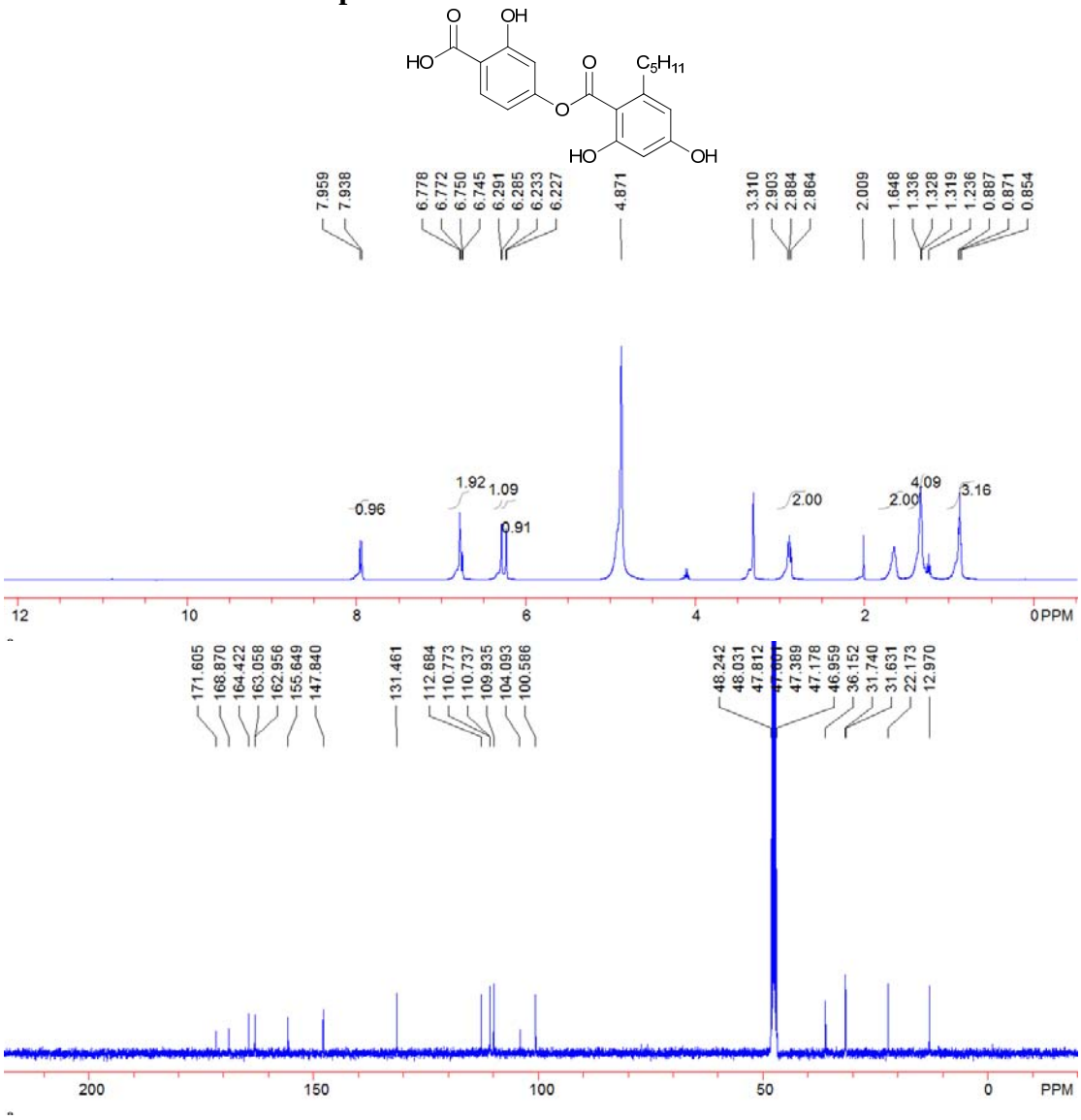
PeakTable

PDA Ch3 220nm 4nm

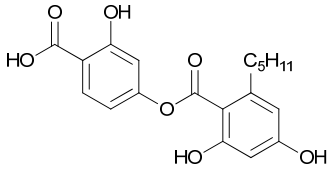
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.958	8208745	3289211	100.000	100.000
Total		8208745	3289211	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-112-1 (MeOH)-redo.lcd

^{1}H and ^{13}C NMR for compound 11b



HPLC for compound 11b



8/17/2013 11:28:10 1 / 1

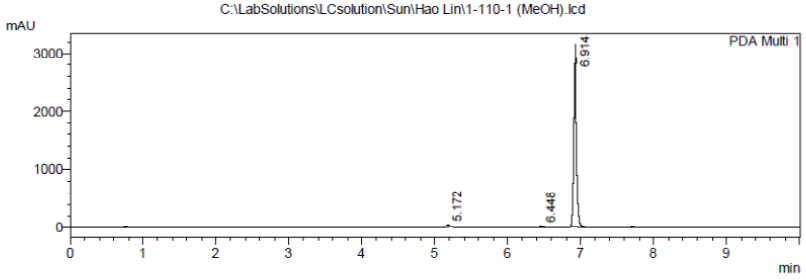
==== Shimadzu LCsolution Analysis Report ====

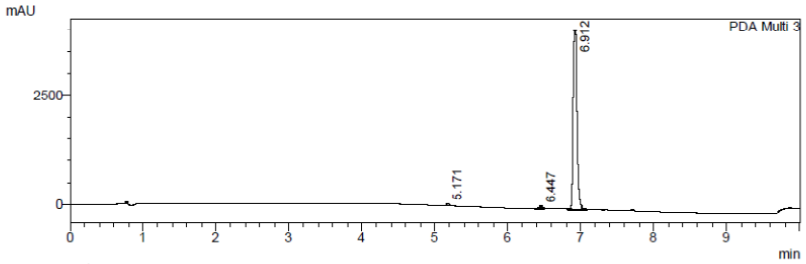
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-110-1 (MeOH).lcd

Sample Name	: 1-110-1 (MeOH)
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-110-1 (MeOH).lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 8/17/2013 11:15:07 AM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-110-1 (MeOH).lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.172	100009	38898	1.222	1.242
2	6.448	62732	23520	0.766	0.751
3	6.914	8022517	3068991	98.012	98.007
Total		8185258	3131409	100.000	100.000

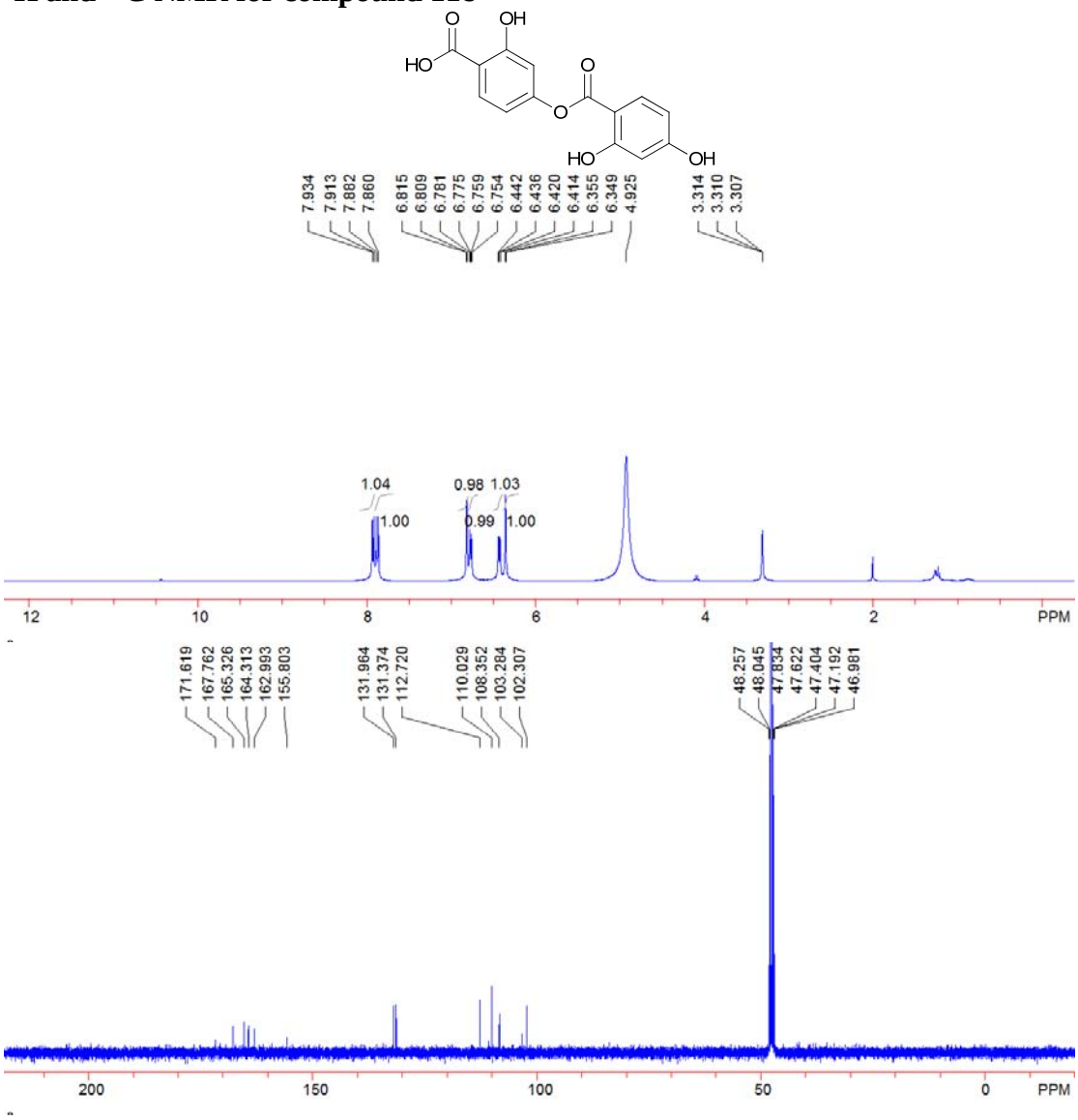
PeakTable

PDA Ch3 220nm 4nm

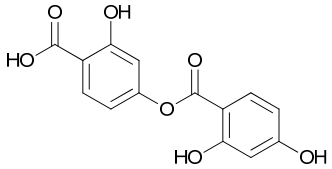
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.171	128001	44342	0.796	1.056
2	6.447	137690	54314	0.856	1.293
3	6.912	15817861	4100444	98.348	97.651
Total		16083553	4199101	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-110-1 (MeOH).lcd

^{1}H and ^{13}C NMR for compound 11c



HPLC for compound 11c



5/2/2013 16:17:38 1 / 1

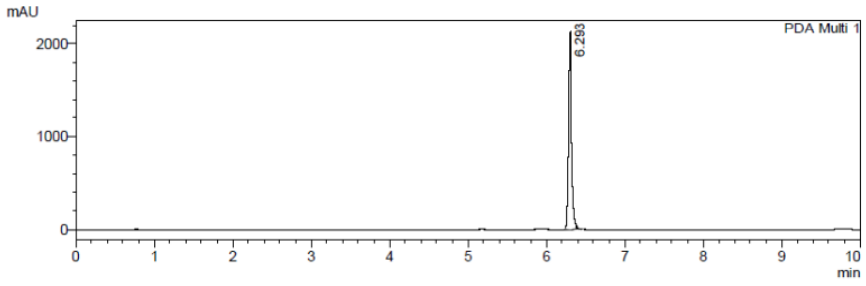
==== Shimadzu LCsolution Analysis Report ====

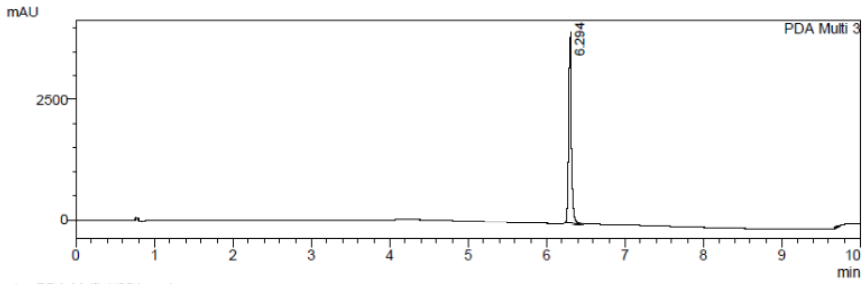
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-116-1.lcd

Sample Name	: 1-116-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-116-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 5/2/2013 3:51:06 PM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-116-1.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.293	5581186	2124937	100.000	100.000
Total		5581186	2124937	100.000	100.000

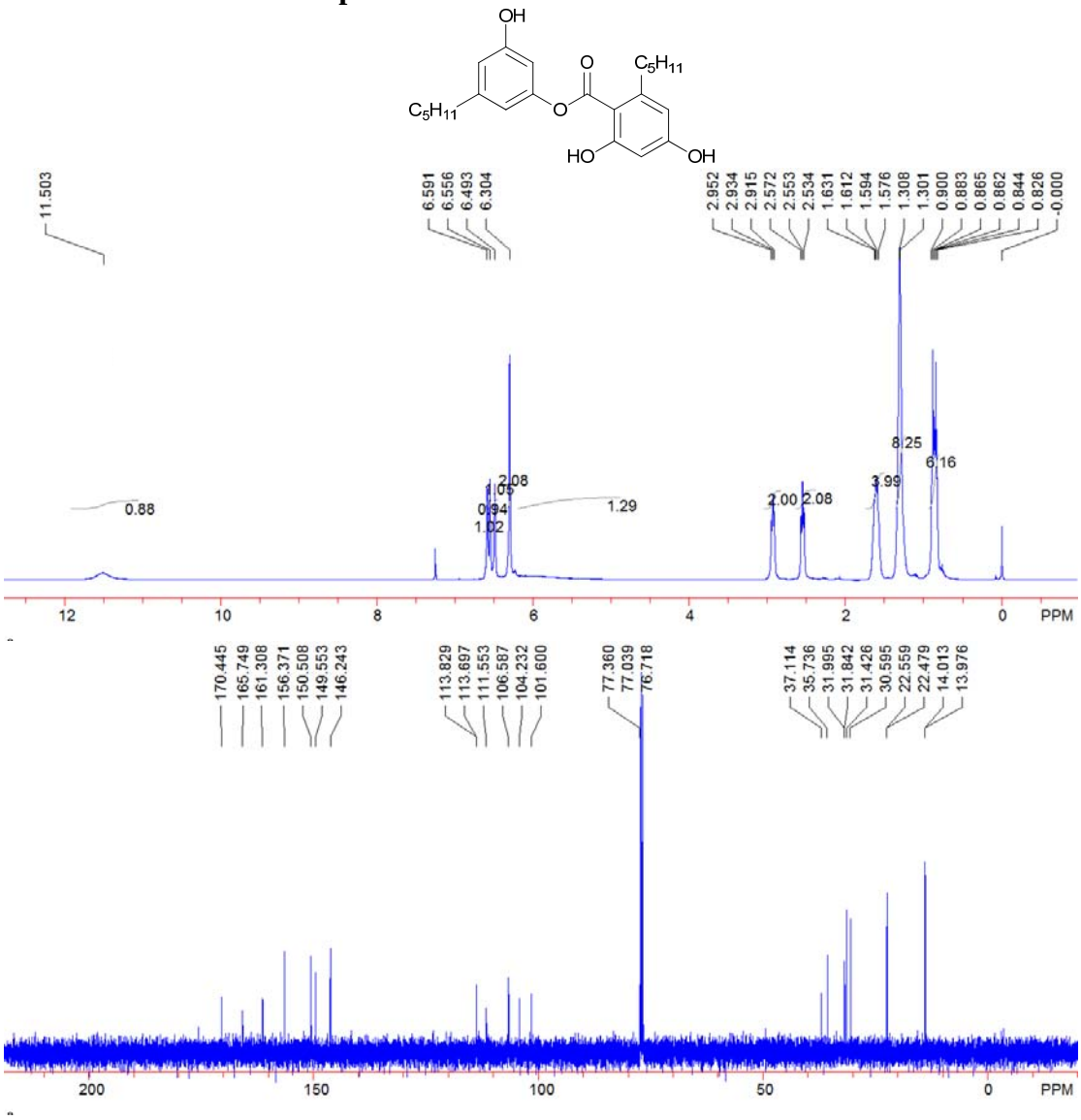
PeakTable

PDA Ch3 220nm 4nm

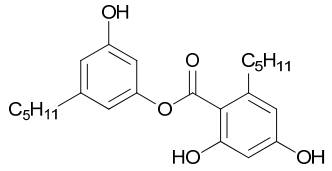
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.294	9916102	4024125	100.000	100.000
Total		9916102	4024125	100.000	100.000

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-116-1.lcd

^{1}H and ^{13}C NMR for compound 11d



HPLC for compound 11d



4/9/2013 10:05:15 1 / 1

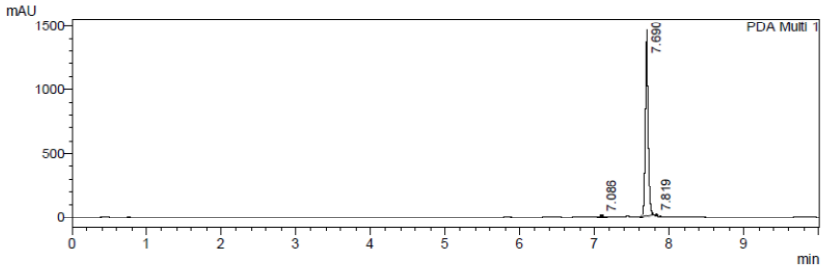
==== Shimadzu LCsolution Analysis Report ====

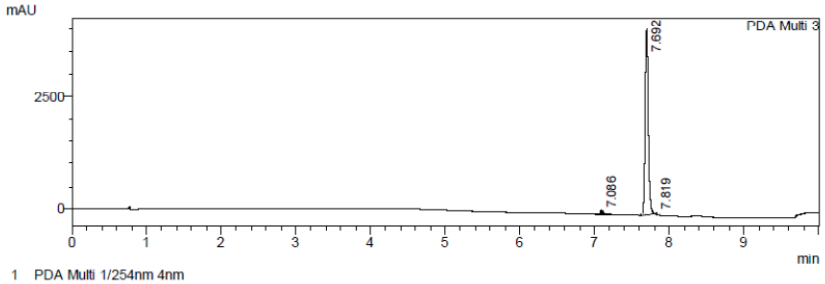
C:\LabSolutions\LCsolution\Sun\Hao Lin\1-96-1.lcd

Sample Name	: 1-96-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 5 uL
Data File Name	: 1-96-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/9/2013 9:47:43 AM

<Chromatogram>

C:\LabSolutions\LCsolution\Sun\Hao Lin\1-96-1.lcd





1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.086	36707	13428	0.908	0.927
2	7.690	3998405	1430289	98.944	98.777
3	7.819	5978	4276	0.148	0.295
Total		4041090	1447992	100.000	100.000

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.086	181897	70014	1.385	1.666
2	7.692	12938391	4121137	98.530	98.087
3	7.819	11138	10343	0.085	0.246
Total		13131426	4201494	100.000	100.000

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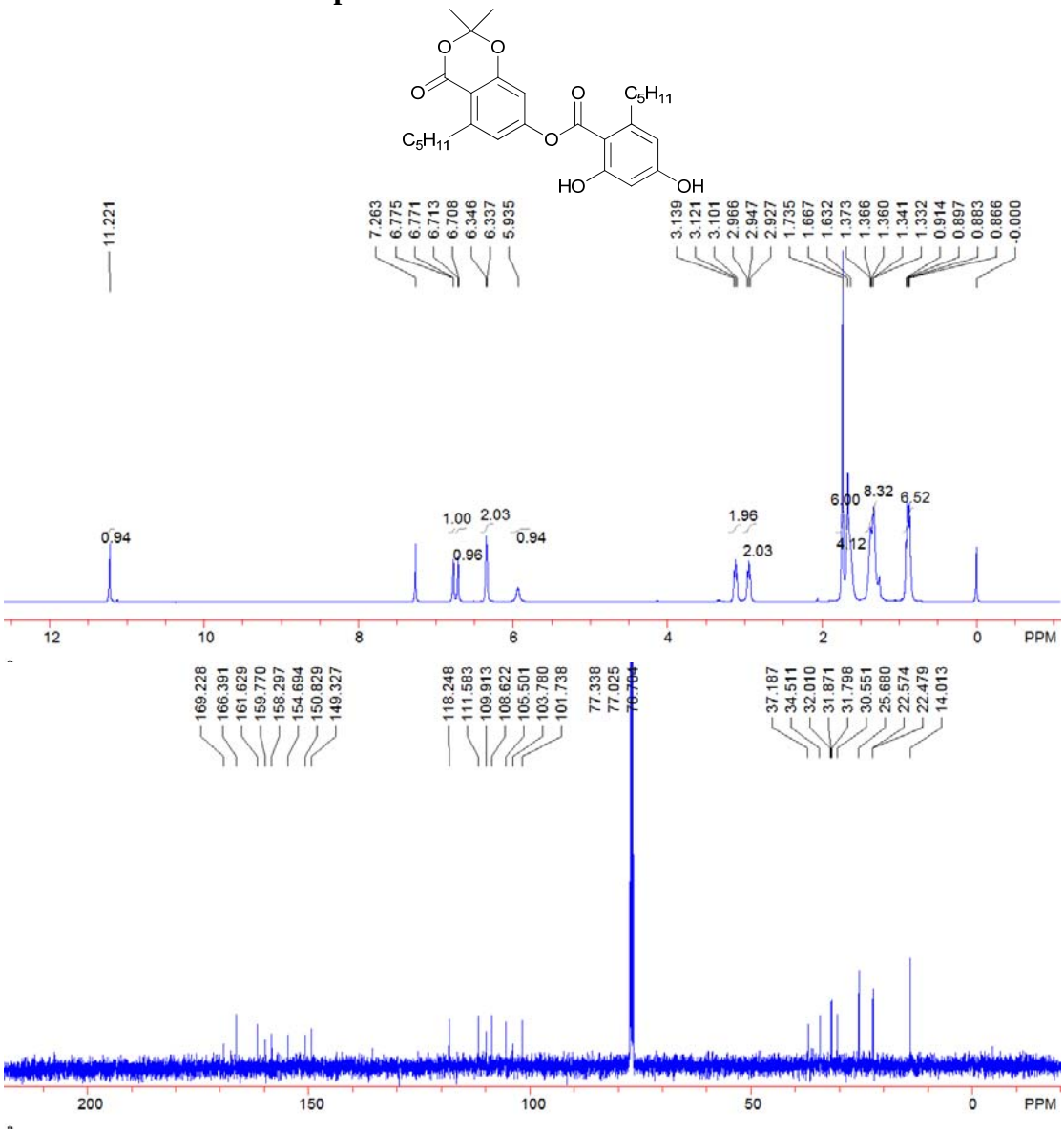
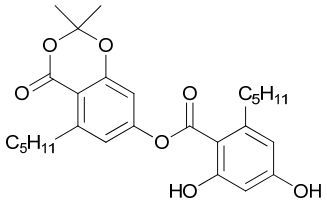
^{1}H and ^{13}C NMR for compound 14



HPLC for compound 14



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==== Shimadzu LCsolution Analysis Report ====

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Sample Name	: 1-114-1
Tray#	: 1
Vail #	: 61
Injection Volume	: 10 uL
Data File Name	: 1-114-1.lcd
Method File Name	: SDQ gradient.lcm
Batch File Name	:
Data Acquired	: 4/28/2013 10:16:42 AM

<Chromatogram>

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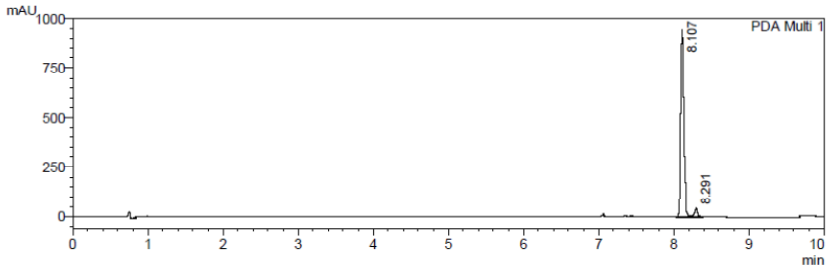

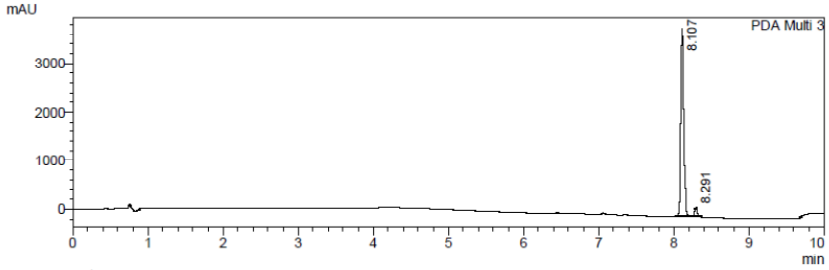

1 PDA Multi 1/254nm 4nm
2 PDA Multi 3/220nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.107	2667242	937828	95.907	95.855
2	8.291	113819	40555	4.093	4.145
Total		2781061	978383	100.000	100.000

PeakTable

PDA Ch3 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.107	10064157	3868953	95.654	95.742
2	8.291	457214	172085	4.346	4.258
Total		10521371	4041038	100.000	100.000

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