Supporting information

A GREEN AND HIGHLY EFFICIENT SYNTHESIS OF 5,5-(PHENYLMETHYLENE)BIS(1,3-DIOXANE-4,6-DIONE) DERIVATIVES IN BIOBASED GLUCONIC ACID AQUEOUS SOLUTION

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1. Measurement

Melting points were measured on XT-4 digital micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a BRUKER AVANCE 400 MHz spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard.^{13}C NMR data were collected on a BRUKER AVANCE 100 MHz instrument with $CDCl_3$ as the solvent and TMS as the internal standard.The analytical MS of the compounds was performed on Agilent LC-MSD Trap VL Apparatus.

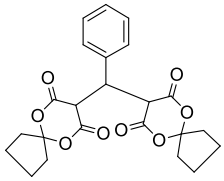
2. General experimental procedure

2.1 General procedure of the preparation of products 3a-3n

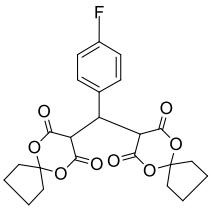
5,5-(Phenylmethylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) **(3a)**: To a 25 mL tube equiped with a stirring bar were added 2,2-butylidene-1,3- dioxane-4,6-dione (**2a**, 2 mmol), aromatic aldehyde (**1a**, 1 mmol) and gluconic acid aqueous solution (4.0 mL). The vessel was then sealed with a screw cap and at room temperature for 5.0 h. Upon completion of the reaction, as confirmed by thin-layer chromatography(petroleum ether/EtOAC 2:1), the reaction mixture was filtered.The filtrate consisting gluconic acid aqueous solution, was recovered and then subjected to the next run in the model reaction.The residue was the crude solid product, then washed with water and purified by recrytallization from absolute ethanol to afford the pure product **3a**. **3b-3n** were synthesized from the same procedure.

3. Spectral data

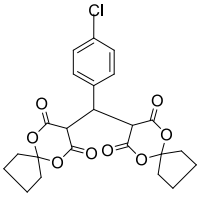
5,5-(Phenylmethylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3a a white solid; mp 156-158°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77-1.84(m, 4 H), 1.86-1.93(m, 4 H), 2.17-2.30(m, 8 H), 4.60-4.68(m, 3 H), 7.28-7.36(m, 3 H), 7.56(d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.62, 24.46, 38.17, 39.08, 39.15, 50.48, 114.50, 127.91, 128.58, 129.01, 140.66, 164.53, 165.59; ESI-MS m/z: 429.2 $[M+H]^+$.



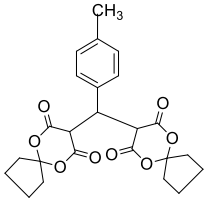
5,5-((4-flurophenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3b a white solid; mp 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78-1.85(m, 4 H), 1.87-1.94(m, 4 H), 2.17-2.31(m, 8 H), 4.56-4.70(m, 3 H), 7.00-7.04(m, 2 H), 7.53-7.57(m, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.61, 24.49, 38.16, 38.46, 39.14, 50.51, 114.58, 115.69, 115.90, 130.53, 130.61, 136.16, 164.50, 165.76; ESI-MS m/z: 466.1$[M+H]^+$.



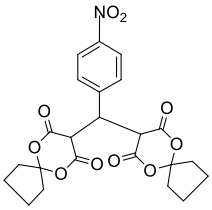
5,5-((4-chlorophenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3c a white solid; mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78-1.85(m, 4 H), 1.87-1.94(m, 4 H), 2.16-2.30(m, 8 H), 4.54-4.70(m, 3 H), 7.30(d, *J* = 8.4 Hz, 2 H), 7.50(d, *J* = 8.4 Hz, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.59, 24.48, 38.16, 38.63, 39.13, 50.33, 114.61, 130.24, 130.84, 138.87, 164.44, 165.66; ESI-MS *m*/*z*: 463.1$[M+H]^+$.



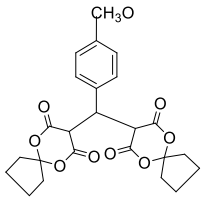
5,5-((4-methylphenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3d a white solid; mp 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77-1.84(m, 4 H), 1.85-1.91(m, 4 H), 2.15-2.28(m, 8 H), 2.32(s, 3 H), 4.55-4.68(m, 3 H), 7.14(d, *J* = 8.0 Hz, 2 H), 7.43(d, *J* = 8.0 Hz, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.07, 22.61, 24.45, 38.14, 38.70, 39.14, 50.56, 114.43, 128.46, 129.63, 137.60, 137.63, 164.58, 165.92; ESI-MS *m*/*z*: 443.2$[M+H]^+$.



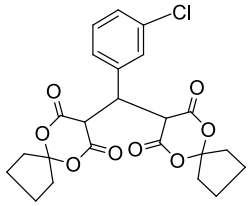
5,5-((4-nitrophenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3e a light yellow solid; mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80-1.87(m, 4 H), 1.89-1.96(m, 4 H), 2.18-2.32(m, 8 H), 4.66-4.79(m, 3 H), 7.77(d, *J* = 8.8 Hz, 2 H), 8.17(d, *J* = 8.8 Hz, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.57, 24.49, 38.16, 39.08, 39.14, 49.92, 114.85, 123.99, 130.07, 147.37, 147.41, 164.31, 165.35; ESI-MS *m*/*z*: 474.1$[M+H]^+$.



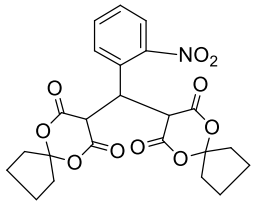
5,5-((4-methoxylphenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3f a light yellow solid; mp 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77-1.84(m, 4 H), 1.86-1.93(m, 4 H), 2.17-2.30(m, 8 H), 4.53-4.70(m, 3 H), 3.78(s, 3 H), 6.85(d, *J* = 8.8 Hz, 2 H), 7.61(d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.61, 24.44, 38.14, 38.40, 39.15, 50.65, 55.24, 114.21, 114.43, 129.86, 132.46, 137.50, 159.05, 164.59, 165.90; ESI-MS *m*/*z*: 459.2[M＋H]$^+$.



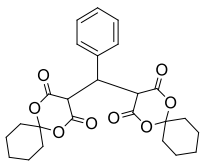
5,5-((3-chlorophenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3g a white solid; mp 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79-1.86(m, 4 H), 1.88-1.95(m, 4 H), 2.17-2.31(m, 8 H), 4.57-4.60(m, 3 H), 7.25-7.31(m, 2 H), 7.45-7.49(m, 2 H), 7.57(s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.60, 24.49, 38.20, 38.85, 39.14, 50.30, 114.64, 127.20, 128.21, 128.60, 130.22, 134.74, 164.37, 165.70; ESI-MS *m*/*z*: 463.1[M＋H]$^+$.



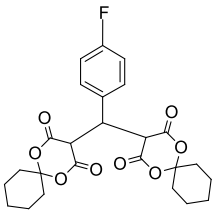
5,5-((2-nitrophenyl)methylene)bis(2,2-butylidene-1,3-dioxane-4,6-dione) 3h a light yellow solid; mp 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80-1.87(m, 4 H), 1.89-1.94(m, 4 H), 2.20-2.28(m, 8 H), 4.52-5.23(m, 3 H), 7.45(t, *J* = 7.2 Hz, 1 H), 7.61(t, *J* = 7.6 Hz, 1 H), 7.78(t, *J* = 7.6 Hz, 1 H), 7.45(t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.59, 24.45, 33.24, 38.19, 39.13, 50.26, 114.56, 124.95, 128.60, 128.69, 133.16, 135.29, 150.12, 163.75, 165.66; ESI-MS *m*/*z*: 474.1[M＋H]$^+$.



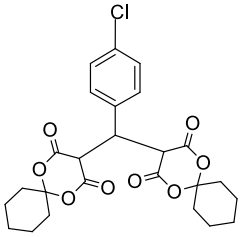
5,5-(Phenylmethylene)bis(2,2-pentylidene-1,3-dioxane-4,6-dione) 3i a white solid; mp 140-142°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45-1.50(m, 4 H), 1.64-1.75(m, 8 H), 1.85-1.88(m, 4 H), 1.96-2.07(m, 4 H), 4.60-4.67(m, 3 H), 7.29(d, *J* = 7.2 Hz, 1 H), 7.35(t, *J* = 7.2 Hz, *J* = 8.0 Hz, 2 H),7.53(d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.85, 22.59, 24.08, 35.54, 37.13, 40.14, 49.42, 106.34, 127.79, 128.41, 128.97, 140.80, 164.02, 165.30; ESI-MS *m*/*z*: 457.2 [M＋H]$^+$.



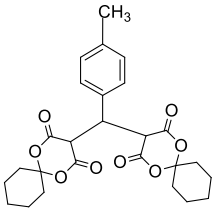
5,5-((4-flurophenyl)methylene)bis(2,2-pentylidene-1,3-dioxane-4,6-dione) 3j a white solid; White solid; mp 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48-1.51(m, 4 H), 1.65-1.77(m, 8 H), 1.89-1.92(m, 4 H), 1.96-2.07(m, 4 H), 4.58-4.65(m, 3 H), 7.01-7.06(m, 2 H), 7.51-7.55(m, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.83, 22.61, 24.06, 35.53, 37.07, 39.47, 49.48, 106.45, 115.68, 115.90, 130.30, 130.38, 136.44, 163.99, 165.59; ESI-MS *m/z*: 475.2$[M+H]^+$.



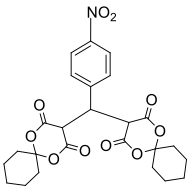
5,5-((4-chlorophenyl)methylene)bis(2,2-pentylidene-1,3-dioxane-4,6-dione) 3k a light yellow solid; mp 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47-1.54(m, 4 H), 1.66-1.77(m, 8 H), 1.89-1.92(m, 4 H), 1.97-2.05(m, 4 H), 4.58-4.63(m, 3 H), 7.31(d, *J* = 8.0 Hz, 2 H), 7.49(d, *J* = 8.0 Hz, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.83, 22.62, 24.06, 35.53, 37.05, 39.60, 49.30, 106.48, 129.08, 130.02, 133.70, 139.24, 163.94, 165.12; ESI-MS *m/z*: 491.1$[M+H]^+$.



5,5-((4-methylphenyl)methylene)bis(2,2-pentylidene-1,3-dioxane-4,6-dione) 3l a white solid; mp 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45-1.50(m, 4 H), 1.65-1.75(m, 8 H), 1.86-1.89(m, 4 H), 1.95-2.05(m, 4 H), 2.32(m, 3 H), 4.56-4.65(m, 3 H), 7.15(d, *J* = 8.0 Hz, 2 H), 7.42(d, *J* = 8.0 Hz, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.08, 21.86, 22.59, 24.09, 35.52, 37.12, 39.75, 49.51, 106.29, 128.29, 129.63, 137.52, 137.80, 164.09, 165.34; ESI-MS *m/z*: 471.2$[M+H]^+$.



5,5-((4-nitrophenyl)methylene)bis(2,2-pentylidene-1,3-dioxane-4,6-dione) 3m a white solid; mp 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47-1.53(m, 4 H), 1.66-1.78(m, 8 H), 1.93-1.96(m, 4 H), 2.01-2.04(m, 4 H), 4.70-4.73(m, 3 H), 7.75(d, *J* = 8.4 Hz, 2 H), 8.20(d, *J* = 8.4 Hz, 2 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.79, 22.63, 24.02, 35.59, 36.95, 40.04, 48.93, 106.76, 124.10, 129.77, 147.33, 147.92, 163.77, 164.82; ESI-MS *m/z*: 502.2$[M+H]^+$.



5,5-((3-chlorophenyl)methylene)bis(2,2-pentylidene-1,3-dioxane-4,6-dione) 3n a white solid; mp 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47-1.52(m, 4 H), 1.67-1.76(m, 8 H), 1.90-1.93(m, 4 H), 2.01-2.03(m, 4 H), 4.55-4.60(m, 3 H), 7.27-7.29(m, 2 H), 7.43-7.45(m, 2 H), 7.56(s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.83, 22.62, 24.06, 35.56, 37.06, 39.81, 49.25, 106.50, 126.97, 128.06, 128.47, 130.19, 134.72, 143.01, 163.85, 165.11; ESI-MS *m*/*z*: 491.1[M＋H]$^{+}$.