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Supporting Information

Syntheses and Characterization of Aryl-Substituted Pyrogallol[4]arenes and Resorcin[4]arenes

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Contents

Synthesis of C-4-methoxyphenylpyrogallol[4]arene (1)

4-methoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 3.05 mL of iodoethane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 8.3 grams of orange liquid.

C-4-methoxyphenylpyrogallol[4]arene: To a round bottom flask, 3.89 grams of pyrogallol and 50 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 3.75 mL of 4-methoxybenzaldehyde was added followed by 0.5 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 1.8 grams of white precipitate. Colourless, plate-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-2-methoxyphenylpyrogallol[4]arene (2)

C-2-methoxyphenylpyrogallol[4]arene: To a round bottom flask, 20.75 grams of pyrogallol and 200 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 20 mL of 2-methoxybenzaldehyde was added followed by 4 mL of concentrated hydrochloric acid. Thec solution was heated to 90°C and refluxed for 8 hours. The

solution was filtered and the powder dried yielding 21.7 grams of purple precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-ethoxyphenylpyrogallol[4]arene (3)

4-ethoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 3.90 mL of iodoethane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 16.2 grams of yellow liquid.

C-4-ethoxyphenylpyrogallol[4]arene: To a round bottom flask, 6.73 grams of pyrogallol and 100 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 7.40 mL of 4-ethoxybenzaldehyde was added followed by 1 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 0.6 grams of white precipitate. Colourless, plate-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-propoxyphenylpyrogallol[4]arene (4)

4-propoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97

grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 4.78 mL of 1-iodopropane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 21.8 grams of yellow liquid.

C-4-propoxyphenylpyrogallol[4]arene: To a round bottom flask, 6.50 grams of pyrogallol and 100 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 8.15 mL of 4-propoxybenzaldehyde was added followed by 1 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 2.7 grams of white precipitate. Pink, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-butoxyphenylpyrogallol[4]arene (5)

4-butoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 5.69 mL of 1-iodobutane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining

liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 17.7 grams of yellow liquid.

C-4-butoxyphenylpyrogallol[4]arene: To a round bottom flask, 18.24 grams of pyrogallol and 250 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 25 mL of 4-butoxybenzaldehyde was added followed by 1 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 3.2 grams of white precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-1-naphthylpyrogallol[4]arene (6)

To a round bottom flask, 10 grams of pyrogallol and 100 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 10.77 mL of 1-naphthaldehyde was added followed by 3 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 2.83 grams of purple precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-methoxy-1-naphthylpyrogallol[4]arene (7)

To a round bottom flask, 6.78 grams of pyrogallol and 125 mL of ethanol were added. The solution was stirred until the pyrogallol dissolved. To the solution, 10 grams of 4-methoxy-1-naphthaldehyde was added followed by 2 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 7.0 grams of purple precipitate. Colourless, prism-shaped crystals were obtained by dissolving powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-methoxyphenylresorcin[4]arene (8)

4-methoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 3.05 mL of iodomethane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 8.3 grams of orange liquid.

C-4-methoxyphenylresorcin[4]arene: To a round bottom flask, 13.36 grams of resorcinol and 100 mL of ethanol were added. The solution was stirred until the resorcinol dissolved. To the solution, 20 mL of 4-methoxybenzaldehyde was added followed by 4 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding about 0.5 grams of white precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-3-methoxyphenylresorcin[4]arene (9)

3-methoxybenzaldehyde: Into 5 grams of 3-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 3-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 3.09 grams of iodomethane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was

rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 10.25 grams of yellow liquid.

*C-3-methoxyphenylresorcin[4]arene***:** To a round bottom flask, 13.36 grams of resorcinol and 100 mL of ethanol were added. The solution was stirred until the resorcinol dissolved. To the solution, 20 mL of 3-methoxybenzaldehyde was added followed by 4 mL of concentrated hydrochloric acid. The solution was heated to 90° and refluxed for 8 hours. The solution was filtered and the powder dried yielding about 0.5 grams of white precipitate. Colourless, plate-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-2-methoxyphenylresorcin[4]arene (10)

C-2-methoxyphenylresorcin[4]arene: To a round bottom flask, 13.36 grams of resorcinol and 100 mL of ethanol were added. The solution was stirred until the resorcinol dissolved. To the solution, 20 mL of 2-methoxybenzaldehyde was added followed by 4 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 0.59 grams of purple precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-ethoxyphenylresorcin[4]arene (11)

4-ethoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten

minutes. To the solution, 3.90 mL of iodoethane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 16.2 grams of yellow liquid.

C-4-ethoxyphenylresorcin[4]arene: To a round bottom flask, 7.92 grams of resorcinol and 100 mL of ethanol were added. The solution was stirred until the resorcinol dissolved. To the solution, 10 mL of 4-ethoxybenzaldehyde was added followed by 6 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 1.24 grams of beige precipitate. Colourless, plate-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-4-isopropoxyphenylresorcin[4]arene (12)

4-isopropoxybenzaldehyde: Into 5 grams of 4-hydroxybenzaldehyde, 125 mL of DMF was added. The reaction was stirred until all 4-hydroxybenzaldehyde dissolved. To the reaction, 1.97 grams of sodium hydride was added and the solution was stirred at room temperature for ten minutes. To the solution, 4.78 mL of 2-iodopropane was added and the solution was stirred at room temperature for one hour. The reaction was quenched with methanol then all solvent was rotovapped off. The product was washed with a 50/50 water/chloroform mixture. Since product dissolves in chloroform, the chloroform layer was removed and rotovapped off. The remaining liquid was dried with magnesium sulfate, filtered, and all remaining solvent was evaporated off yielding 28.41 grams of yellow liquid.

C-4-isopropoxyphenylresorcin[4]arene: To a round bottom flask, 6.97 grams of resorcinol and 100 mL of ethanol were added. The solution was stirred until the resorcinol dissolved. To the solution, 10 mL of 4-isopropoxybenzaldehyde was added followed by 6 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 0.19 grams of white precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in DMSO and allowing the solution to slowly evaporate.

Synthesis of C-1-naphthylresorcin[4]arene (13)

C-4-naphthylresorcin[4]arene: To a round bottom flask, 10 grams of resorcinol and 100 mL of ethanol were added. The solution was stirred until the resorcinol dissolved. To the solution, 12.33 mL of 4-naphthaldehyde was added followed by 3 mL of concentrated hydrochloric acid. The solution was heated to 90°C and refluxed for 8 hours. The solution was filtered and the powder dried yielding 13.3 grams of brown precipitate. Colourless, prism-shaped crystals were obtained by dissolving the powder in pyridine and allowing the solution to slowly evaporate.