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Electronic Supplementary Information to:

Conversion of 2-(4-carboxyphenyl)-6-nitrobenzothiazole to 4-(6-amino-5-hydroxybenzothiazol-2-yl)benzoic acid by a recombinant *E. coli*

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Experimental:

1. 2-(4-Carboxyphenyl)benzothiazole:

A mixture of 2-aminothiophenol (9.00 ml, 0.08 mol), 4-carboxybenzaldehyde (10.1 g, 0.07 mol) and DMSO (40 mL) was heated to 145^{o}C, and held at this temperature for 3.5 hours. The reaction mixture was diluted with water and separated solids were collected, dried and recrystallized from acetic acid; 14.15g, (82% yield), white solid, m.p. 294.1-295.5^{o}C. **Mass Spectrum:** m/z, 255 (M^{+}), 238 (M-OH), 210 (M-COOH), 108. **FT-IR** (KBr; cm^{-1}): 3051 (br; OH), 1684 (CO), 1609, 1424, 1407, 1291, 970, 756. **Anal. Calcd** for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49; S, 12.56%. **Found:** C, 65.71; H, 3.96; N, 5.30; S, 12.66%. NMR: not available due to poor solubility.

2. 2-(4-Carboethoxyphenyl)benzothiazole:

A mixture of 2-(4-carboxyphenyl)benzothiazole (3.0g, 0.012 mol), and DMF (60 mL), was cooled to 10^{o}C in an ice bath. Potassium carbonate (3.87g, 0.028 mol), and bromoethane (5.5 mL, 0.072 mol) were added, and the reaction mixture was stirred for 48 hours at room temperature. The mixture was then poured into water, and the separated solids were filtered, washed with water, and the crude product was recrystallized from ethanol. The desired product, 1.34g, (40% yield) was obtained as a gray solid, m.p. 131.3- 132.3^{o}C. **Mass Spectrum:** m/z, 283 (M^{+}), 255 (M- C_2H_4), 238 (M-OEt), 210 (238- CO), 183, 139, 105. **FT-IR (KBr; cm^{-1}):** 3100 (sp^2C-H), 2989 (sp^3C-H), 1710 (C=O), 1522 (asym NO_2), 1341 (sym NO_2), 1279 (C-O-C), 1108, 773, 753, 696. **^{1}H NMR ($CDCl_3$; δ in ppm):** 1.45 (t, 3H, methyl), 4.45 (q, 2H, OCH_2), 7.4-7.55 (m, 2 ArH), 7.9 (d, 1 ArH), 8.05- 8.20 (m, 5 ArH). **^{13}C NMR ($CDCl_3$; δ in ppm):** 14.76, 61.72 (sp^3 C), 122.12, 123.99, 126.09, 126.99, 127.78, 130.61, 132.79, 135.67, 137.74,

154.51, 166.32 (sp^2C). **Anal.Calcd for $C_{16}H_{13}NO_2S$:** C, 67.83; H, 4.62; N, 4.94. **Found:** C, 67.87; H, 4.32; N, 4.23.

3. 2-(4-Carboethoxyphenyl)-6-nitrobenzothiazole:

To nitric acid (sp.gr.1.49, 90%, 80 mL), 2-(4-carboxyphenyl)benzothiazole (10.00g) was added in portions, the mixture was stirred at room temperature for 1 hour, diluted with water and the crude product, 11.64g (99% yield), was collected by filtration. To a mixture of this acid (10g, 0.03 mol), potassium carbonate (9.20g, 0.07 mol) and DMF (270 mL) was added 1-bromoethane (14 mL, 0.18 mol), and the mixture was stirred at room temperature for 72 hours. The crude product obtained as a solid on dilution with water was collected and transferred to a column of silica gel. Elution with toluene followed by recrystallization from ethanol gave pure ester, 6.38g (58% yield), m.p. 204-206^{o}C. **Mass spectrum:** m/z, 328 (M^+), 300 (M-C_2H_4), 283 (M-OEt), 237 (M-NO_2), 209(237-CO). IR (cm^{-1}): 3094 (sp^2C-H), 2987 ((sp^3C-H)), 1710 (C=O), 1522 (asym. NO_2), 1340 (sym. NO_2), 1278 (C-O-C), 1108. **^{1}H NMR ($CDCl_3$; δ in ppm):** 1.42, 1.44, 1.47 (t, 3H, methyl), 4.40, 4.42, 4.45, 4.48 (q, 2H, OCH_2), 8.16,8.18 (d, 1H, peri ArH), 8.19 (s, 4 ArH), 8.37, 8.38, 8.40, 8.41 (d,d, 1 ArH), 8.86, 8.87 (d, 1 ArH). **^{13}C NMR ($CDCl_3$; δ in ppm):** 14.40, 61.51 (sp^3C), 118.33, 122.10, 123.77, 127.80, 130.39, 133.50, 135.52, 136.27, 145.20, 157.66, 165.61, 172.32. **Anal. Calcd for $C_{16}H_{12}N_2O_4S$:** C, 58.53; H, 3.68; N, 8.53; S, 9.77%. **Found:** C, 58.68; H, 3.71; N, 8.24; S, 9.94%.

4. 2-(4-Carboxyphenyl)-6-nitrobenzothiazole:

A mixture of 2-(carboethoxyphenyl)-6-nitrobenzothiazole (3.44g, 0.011 mol), THF (200 mL), and sodium hydroxide (1.24g, 0.032 mol) was kept at reflux for 18 hours, cooled, and acidified to pH 2, and the separated solid was recrystallized from acetic acid. The product, 2.54g (81%), did not melt below 350^{o}C. **Mass spectrum:** m/z 300 (M^+), 270 (M-NO), 255(M-COOH), 242 (270-CO), 209 (255-NO_2). **FT-IR (KBr; cm^{-1}):** 3101 (sp^2-C-H), 1695 (C=O), 1517 (asym. NO_2), 1346 (sym. NO_2), 1293 (C-O-C), 784. **Anal. Calcd for $C_{14}H_8N_2O_4S$:** C, 56.00; H, 2.69; N, 9.33; S, 10.68%. **Found:** C, 55.15; H, 2.70; N, 9.13; S, 10.54%.