

## Supporting Information

### Synthesis of catechol-NHS

[2-(3,4-Dihydroxy-phenyl)-ethyl]-carbamic acid 2,5-dioxo-pyrrolidin-1-yl ester (catechol-NHS; **1**) was prepared according to the procedure of Wilchek and coworkers (1). A solution of dopamine hydrochloride (190 mg, 1 mmol) in DMF (2 mL) was added dropwise over 30 min to a solution of disuccinimidyl carbonate (512 mg, 2 mmol) in DMF (15 mL), followed by slow addition of triethylamine (277  $\mu$ L, 2 mmol) while stirring. After 60 min, the solvent was partially evaporated (to 5 mL), 1N HCl (30 mL) was added, and the solution was extracted with EtOAc (30 mL). Evaporation of the organic phase to dryness and crystallization from EtOAc afforded a crystalline carbonated side product, [2-(2-Oxo-benzo[1,3]dioxol-5-yl)-ethyl]-carbamic acid 2,5-dioxo-pyrrolidin-1-yl ester (**2**) (27% yield) and the clean product **1** (64% yield) in the solution.

**1**:  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.59 (t,  $J$  = 6.2 Hz, 2H,  $\text{PhCH}_2$ ), 2.76 (s, 4H,  $\text{CH}_2\text{CH}_2$ ), 3.19 (q,  $J$  = 6.2 Hz, 2H,  $\text{CH}_2\text{N}$ ), 6.45 (d,  $J$  = 7.8 Hz, 1H, Ph), 6.59 (s, 1H, Ph), 6.64 (d,  $J$  = 7.8 Hz, 1H, Ph), 8.33 (bt, 1H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  25.5 ( $\text{CH}_2\text{CH}_2$ ), 34.5 ( $\text{CH}_2\text{Ph}$ ), 42.8 ( $\text{CH}_2\text{N}$ ), 115.5, 115.9, 119.2, 129.3, 143.6, 145.1 (Ph), 151.7 ( $\text{NCO}_2$ ), 171.2 (CON). MS  $m/z$  333 ( $\text{MK}^+$ , 100), 317 ( $\text{MNa}^+$ , 59), 295 ( $\text{MH}^+$ , 6), 238 (92). TLC (E. Merck 0.2 mm pre-coated silica 60 plates)  $R_f$  (EtOAc) 0.24.

**2**:  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.76 (s, 4H,  $\text{CH}_2\text{CH}_2$ ), 2.85 (t,  $J$  = 7.2 Hz, 2H,  $\text{PhCH}_2$ ), 3.32 (td,  $J$  = 7.2, 5.7 Hz, 2H,  $\text{CH}_2\text{N}$ ), 7.15 (dd,  $J$  = 8.2, 1.8 Hz, 1H, Ph), 7.35 (d,  $J$  = 1.8 Hz, 1H, Ph), 7.36 (d,  $J$  = 8.2, 1H, Ph), 8.35 (t,  $J$  = 5.7, 1H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  25.3 ( $\text{CH}_2\text{CH}_2$ ), 34.5 ( $\text{CH}_2\text{Ph}$ ), 42.5 ( $\text{CH}_2\text{N}$ ), 110.0, 110.7, 125.0, 136.0, 141.5, 143.0

(Ph), 151.0 (CO<sub>3</sub>), 151.7 (NCO<sub>2</sub>), 170.5 (CON). MS *m/z* 359 (MK<sup>-</sup>, 37), 321 (MH<sup>+</sup>, 100), 306 (64) 254 (59), 253 (97), 243 (64), 238 (76), 234 (62).

- (1) Morpurgo, M., Bayer, E.A., and Wilchek, M. (1999) N-hydroxysuccinimide carbonates and carbamates are useful reactive reagents for coupling ligands to lysines on proteins. *J. Biochem. Biophys. Methods* 38, 17-28.