**Figure S1**

5 7 1

(A) (B) (C)

234

(D) (E) (F)

68

(G) (H)

Figure S1. Binding modes of (2R,3R,11bR)-13a (A), (2S,3R,11bR)-13a (B), (2R,3S,11bR)-13a (C), (2S,3R,11bS)-13a (D), (2S,3S,11bR)-13a (E), (2R,3R,11bS)-13a (F), (2S,3S,11bS)-13a (G), (2R,3S,11bS)-13a (H) into VMAT2. Hydrogen bonds and hydrophobic interactions are shown as green dashed lines and red “eyelashes”, respectively.

The 2D plots are generated using LIGPLOT v2.2.4 [1].

[1] Laskowski, R. A.; Swindells, M. B., LigPlot+: Multiple Ligand–Protein Interaction Diagrams for Drug Discovery. Journal of Chemical Information and Modeling 2011, 51 (10), 2778-2786.

**Figure S2**

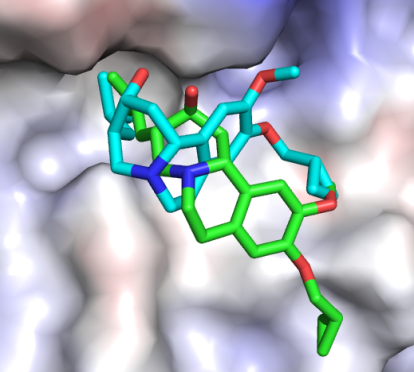


Figure S2. The bindings of compounds and VMAT2. Cyan: (2R, 3S, 11bR)-13a; green: (2S, 3S, 11bR)-13a.

**Figure S3**

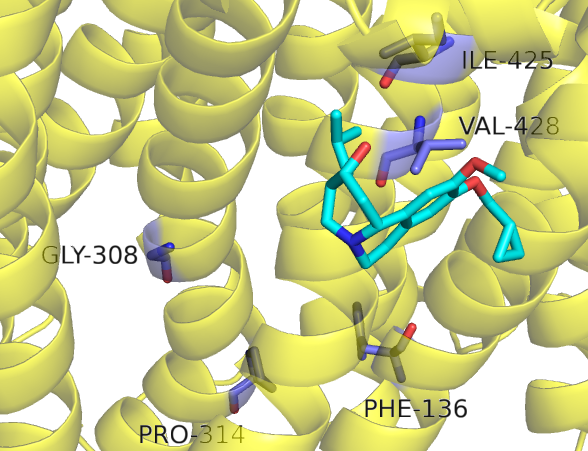


Figure S3. 3D structure of VMAT2. The protein and key residues were shown in yellow cartoon and blue sticks, and the compound (2R, 3S, 11bR)-13a was shown in cyan sticks.