**Fig S1.** **Schematic representation of sample preparation and chemical enhancement using 1,2 Indandione.** A: Representative optical image of the surface of deposition namely two rectangles of papers, one white and one red. Six such surfaces were prepared, 1 set for DESI MSI and 1 for MALDI MSI, both after chemical enhancement. A fingermark was placed in the middle of each surface of deposition to generate half mark on white paper and half mark on red paper. For each set, a natural control mark (CNT), a mark contaminated with risperidone (RIS) and a mark contaminated with risperidone and paliperidone (RIS/PAL) in a physiological ratio were deposited.

**Fig S2**. **MALDI MSI of a natural fingermark spotted with a serial dilution of risperidone (A) and paliperidone (C).** Risperidone and paliperidone were detected and imaged at *m/z* 411.21973 (A in green) and 427.21503 (B in green), respectively and overlaid with the image of an endogenous ion at *m/*z 368.42642, reconstructing the fingerprint ridge pattern (red). The average mass spectra extracted from the ROI of the spots at 0.1, 1 and 10 ng/mL for both risperidone and paliperidone are also reported in panels B and D respectively showing the LOD for risperidone at 1 ng/mL and the LOD for paliperidone at 10 ng/mL.