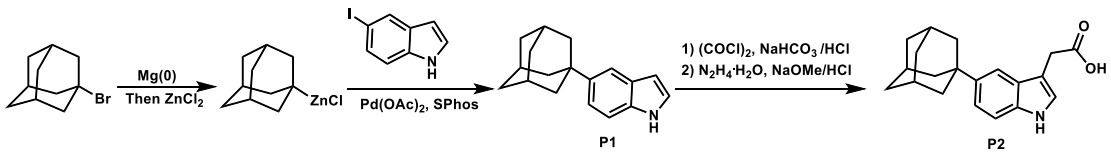

Figure S1. Schematic of the synthesis of 5-adamantyl-IAA (P2).

The procedure of **P1** synthesis:

A dry, argon flushed Schlenk-flask equipped with a magnetic stirring bar and a septum was charged with LiCl (187 mg, 4.4 mmol, 1.1 equiv) and heated with a heat gun under a high vacuum (5 min). After cooling to room temperature, magnesium turnings (194 mg, 8.0 mmol, 2 equiv) were added, followed by THF (10 mL). The magnesium was activated using 1,2-dibromoethane (38 mg, 0.2 mmol, 5 mol%) and TMSCl (22 mg, 0.2 mmol, 5 mol%). After cooling to 0°C, $ZnCl_2$ (600 mg, 4.4 mmol, 1.1 equiv) was added followed by the 1-bromoadamantane (861 mg, 4.0 mmol, 1 equiv). The reaction mixture was stirred at 25°C for 5 h. Then 5-iodo-1*H*-indole (875 mg, 3.6 mmol, 0.9 equiv) was added to the freshly prepared zinc reagent followed by $Pd(OAc)_2$ (9 mg, 0.04 mmol, 1 mol%) and SPhos (33 mg, 0.08 mmol, 2 mol%) and the mixture was stirred at 50°C for 5 h. The reaction mixture was quenched with sat. NH_4Cl solution (10 mL) and extracted with EtOAc (3×20 mL). The combined organic phases were dried over Na_2SO4 and concentrated in vacuo. The crude residue obtained was purified by flash column chromatography to give the pure product **P1** (white solid, 610 mg, 60% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (br s, 1H), 7.62 (dt, *J* = 1.8, 0.8 Hz, 1H), 7.35 (dt, *J* = 8.6, 0.9 Hz, 1H), 7.28 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.18 (dd, *J* = 3.2, 2.4 Hz, 1H), 6.53 (ddd, *J* = 3.0, 2.0, 0.8 Hz, 1H), 2.16 – 2.08 (m, 3H), 2.00 (d, *J* = 2.8 Hz, 6H), 1.79 (m, 6H).

The procedure of **P2** synthesis:

A dry, argon flushed flask equipped with a magnetic stirring bar was charged with **P1** (502 mg, 2.0 mmol, 1.0 equiv) in THF (10 mL), freshly distilled oxalyl chloride (279 mg, 2.2 mmol, 1.1 equiv) in anhydrous THF (2 mL) was added dropwise over 10 min at 0°C. An orange precipitate formed. Sat. aq $NaHCO_3$ (5 mL) was then added with caution, and the mixture was heated at reflux for 30 min, then cooled and acidified with 10% HCl; this resulted in the precipitation of the substituted indole-3-glyoxalic acid, which was filtered and dried. Hydrazine hydrate (320 mg, 10 mmol, 5 equiv) was added to a solution of substituted indole-3-glyoxalic acid in 2-methoxyethanol (5 mL). The temperature of the mixture was increased to 60°C and NaOMe (1.08 g, 20 mmol, 10 equiv) was added portion-wise. The mixture was slowly heated at 150°C, whereby MeOH, H_2O, hydrazine, and part of the solvent were evaporated. The mixture was kept at 150°C for 1 h, cooled, and poured onto crushed ice. The aqueous layer was extracted with EtOAc and acidified with concentrated HCl at 0°C. The oil that formed was extracted with EtOAc. The EtOAc solution was washed with H_2O, dried over $MgSO_4$, and evaporated in vacuo. The crude product obtained was further purified by the preparation HPLC to afford the desired pure product **P2** (white solid, 216 mg, 35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (br s, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.30 (d, *J* = 1.4 Hz, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 2H), 2.16 – 2.08 (m, 3H), 2.00 (d, *J* = 2.8 Hz, 6H), 1.80 (m, 6H).