Catalytic experiments using complex 3.
In a typical experiment, indole (0.07 mmol) was added to a CD$_3$CN solution (0.5 ml) of allyl alcohol (4.8 μl, 0.07 mmol) and catalyst (3) (0.0023 g, 0.0035 mmol) in an oven-dried 5 mm NMR tube. The allyl alcohol was monitored by $^1$H NMR spectroscopy at 296 K. Modifications to these experimental conditions are reported in the table. It is essential that indole is the last reagent added, otherwise significantly lower conversions are obtained.

Catalytic experiments using the Trost catalyst modified with HBF$_4$·Et$_2$O.
Indole (0.07 mmol) was added to a CD$_3$CN solution (0.5 ml) of allyl alcohol (4.8 μl, 0.07 mmol), the Trost catalyst (4) (0.0018 g, 0.0035 mmol) and HBF$_4$·Et$_2$O (0.00057 g, 0.0035 mmol, introduced as a stock solution in CD$_3$CN) in an oven-dried 5 mm NMR tube. The allyl alcohol was monitored by $^1$H NMR spectroscopy at 296 K. Under these conditions, full conversion was obtained after 23 minutes with the 3-allylindole/1,3-diallylindole ratio = 9:1. The use of 4 equivalents of the acid with respect to the Trost catalyst resulted in the formation of a noticeable amount of unidentified byproducts.

Synthesis of 3-allyl-2-phenylindole (6a) and 1,3-diallyl-2-phenylindole (6b).
2-Phenylindole (0.1933 g, 1 mmol) was added to an acetonitrile solution (7 ml) of allyl alcohol (68.0 μl, 1 mmol) and catalyst (3) (0.0325 g, 0.05 mmol) in an oven-dried flask under nitrogen. The reaction mixture was stirred at room temperature for 55 min. Evaporation of the volatiles in vacuo and separation of the remainder by column chromatography (SiO$_2$, pentane/dichloromethane = 5:1) afforded 3-allyl-2-phenylindole (6a) (0.2005 g, 86%) as a yellowish powder and 1,3-diallyl-2-phenylindole (6b) (0.0125 g, 5%) as a transparent oil.

6a: $^1$H NMR (CDCl$_3$, 300.13 MHz): $\delta$ = 3.67 (2H, dt, $J_1 = 5.7$, $J_2 = 1.5$), 5.11 (1H, t, $J = 1.8$), 5.16 (1H, dq, $J_1 = 6.9$, $J_2 = 1.8$), 6.11-6.23 (1H, m), 7.17 (1H, td, $J_1 = 7.4$, $J_2 = 0.9$), 7.25 (1H, td, $J_1 = 7.5$, $J_2 = 0.9$), 7.38-7.66 (7H, m), 8.09 (1H, s); $^{13}$C NMR (CDCl$_3$, 75.47 MHz): $\delta$ = 29.3, 110.9, 111.1, 115.5, 119.8, 120.0, 122.7, 128.0, 128.2, 129.2, 129.7, 133.4, 135.2, 136.3, 137.7.

6b: $^1$H NMR (CDCl$_3$, 300.13 MHz): $\delta$ = 3.47 (2H, d, $J = 6.0$), 4.63 (2H, m), 4.91-5.17 (4H, m), 5.87-6.12 (2H, m), 7.17 (1H, $t$, $J = 7.7$), 7.26 (1H, $t$, $J = 7.3$), 7.35 (1H, d, $J = 8.4$), 7.43-7.51 (5H, m), 7.66 (1H, d, $J = 7.8$); $^{13}$C NMR (CDCl$_3$, 75.47 MHz): $\delta$ = 29.6, 46.8, 110.4, 111.3, 114.9, 116.6, 119.69, 119.72, 122.1, 128.4, 128.5, 128.6, 130.8, 132.2, 134.3, 137.1, 138.3, 138.4.
Synthesis of 3-allyl-1-methyl-2-phenylindole (7).

1-Methyl-2-phenylindole (0.2073 g, 1 mmol) was added to an acetonitrile solution (7 ml) of allyl alcohol (68.0 μl, 1 mmol) and catalyst (3) (0.0325 g, 0.05 mmol) in an oven-dried flask under nitrogen. The reaction mixture was stirred at room temperature for 30 min. Evaporation of the volatiles in vacuo, filtration of a dichloromethane solution of the remainder through a plug of SiO₂ (5x1 cm) afforded 3-allyl-1-methyl-2-phenylindole (7) (0.2365 g, 96%) as a transparent oil.

¹H NMR (CDCl₃, 400.13 MHz): δ = 3.48 (2H, d, J = 6.0), 3.65 (3H, s), 5.03 (1H, dd, J₁ = 10.2, J₂ = 1.5), 5.08 (1H, dd, J₁ = 17.2, J₂ = 1.5), 5.99-6.12 (1H, m), 7.17 (1H, td, J₁ = 7.8, J₂ = 0.9), 7.29 (1H, td, J₁ = 7.2, J₂ = 0.9), 7.37-7.55 (6H, m), 7.66 (1H, d, J = 7.8);

¹³C NMR (CDCl₃, 75.47 MHz): δ = 29.6, 31.2, 109.7, 111.0, 114.9, 119.57, 119.63, 122.1, 128.1, 128.3, 128.7, 130.9, 132.2, 137.7, 138.3, 138.5.