Supporting Information

The 3-Aza π-Allyl Palladium Derived from Imino Migration in Palladium-Carbene: an MCRs Toward 3-Arylamino Indole

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1. General considerations.

All reactions were performed under indicated atmosphere (if not specified, it was performed under air) in a sealed tube. All solvents were distilled prior to use. The boiling point of petroleum ether is between 60 and 90 °C. THF, and dioxane were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN were distilled from CaH₂. The water used in reaction was distilled water. For chromatography, 300-400 mesh silica gel (Qingdao, China) was employed. ¹H and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet IS5 infrared spectrometer. HMRS were obtained on a 6540 UHD Accurate-Mass Q-TOF LC/MS.

2. The procedures for the synthesis of substrates.

The preparation of 2-iodoaniline derivatives was followed by literature procedure.[¹]

The preparation of aldehyde hydrazones was followed by literature procedure.[²]

The preparation of aryl isonitriles was followed by literature procedure.[³]

3-1. Typical procedure for PdCl₂(dppf)·CH₂Cl₂-catalyzed reactions of N-methyl 2-iodoaniline derivatives with aldehyde hydrazones and aryl isonitriles:
PdCl₂(dppf)·CH₂Cl₂ (8.2 mg, 0.01 mmol), PPh₃ (7.9 mg, 0.03 mmol), LiO'Bu (48.0 mg, 0.6 mmol), N-methyl 2-iodoaniline derivative 1 (0.2 mmol), aryl isonitrile 2 (0.3 mmol), aldehyde hydrazone 3 (0.4 mmol) was added to a sealed tube, THF (3 mL) and water (0.5 mL) was added via syringe. Then the tube was sealed and the mixture was stirred at 100 °C for 5 hours, and then at room temperature for 10 hours. After the reaction ended, solution was extracted by ethyl acetate and the combined extract was removed in vacuo to leave a residue which was purified by flash silica gel chromatography to afford pure product 4.

3-2. Typical procedure for Pd₂(dba)₃·CHCl₃-catalyzed reactions of 2-iodoaniline with aldehyde hydrazones and aryl isonitrile: Pd₂(dba)₃·CHCl₃ (5.2 mg, 0.005 mmol), PPh₃ (7.9 mg, 0.03 mmol), LiO'Bu (48.0 mg, 0.6 mmol), 2-iodoaniline (43.8 mg, 0.2 mmol), aryl isonitrile 2a (56.2 mg, 0.3 mmol), aldehyde hydrazone 3 (0.4 mmol) was added to a sealed tube, dioxane (3 mL) and water (0.5 mL) was added via syringe. Then the tube was sealed and evacuated to a vacuum of 15 mmHg and purged with oxygen. The mixture was stirred at 100 °C for 5 hours. After the reaction ended, solution was extracted by ethyl acetate and the combined extract was removed in vacuo to leave a residue which was purified by flash silica gel chromatography to afford pure product 5.
3-3. Typical procedure for PdCl$_2$(dppf)-CH$_2$Cl$_2$-catalyzed four-component reaction of 2-iodoaniline with aldehyde hydrazone, aryl isonitrile and acetone: PdCl$_2$(dppf)-CH$_2$Cl$_2$ (8.2 mg, 0.01 mmol), PPh$_3$ (7.9 mg, 0.03 mmol), LiO'Bu (48.0 mg, 0.6 mmol), 2-iodoaniline (43.8 mg, 0.2 mmol), aryl isonitrile 2a (56.2 mg, 0.3 mmol), aldehyde hydrazone 3a (109.7 mg, 0.4 mmol) was added to a sealed tube, Acetone (3 mL) and water (0.5 mL) was added via syringe. Then the tube was sealed and the mixture was stirred at 100 °C for 5 hours. After the reaction ended, solution was extracted by ethyl acetate and the combined extract was removed in vacuo to leave a residue which was purified by flash silica gel chromatography to afford pure product 6a.

Besides the mechanism that has been proposed in Scheme 1, Eq.4 and Scheme 2, (refer to as mechanism a), there is another controversial pathway that may be considered (mechanism b).

Mechanism b

In mechanism b, transimination between the aniline and aryl hydrazone starting materials provides an iminium intermediate G. Then, oxidative addition ArI to Pd(0) and insertion into the isocyanide took place to form the intermediate H. After that, the intramolecular migratory insertion into the iminium followed by β-hydride elimination regenerates the Pd(0) catalyst and forms iminium intermediate F. Finally, the deproton of F took place to produce 5, or the iminium F was attacked by H$_2$O or acetone to provide product 4 or 6a.

To either support or rule out this potential mechanism, we tested the reaction under
the same conditions using N-(2-iodophenyl)-1-phenylmethanimine and phenylisocyanide 2a (S1). However, no compounds 5 was detected, which ruled out the possibility of this pathway.

Thus, we consider the mechanism described in Scheme 1, Eq. 4 and Scheme 2 is most plausible with the information currently available, although vigorous experiments are needed to unambiguously establish this mechanism.

5. Spectra Data.

3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4a)
Yellow solid. m.p.: 83-84 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.50 (d, \( J = 7.5 \) Hz, 2 H), 7.39-7.34 (m, 3 H), 7.29 (t, \( J = 7.6 \) Hz, 1 H), 7.16-7.08 (m, 3 H), 6.65 (d, \( J = 8.0 \) Hz, 1 H), 6.39 (t, \( J = 7.6 \) Hz, 1 H), 6.26 (d, \( J = 7.6 \) Hz, 1 H), 3.53 (s, 1 H), 2.90-2.83 (m, 4 H), 2.30 (hept, \( J = 6.8 \) Hz, 1 H), 1.18 (d, \( J = 6.8 \) Hz, 3 H), 0.98 (d, \( J = 6.8 \) Hz, 3 H), 0.82 (d, \( J = 6.8 \) Hz, 3 H), 0.74 (d, \( J = 6.8 \) Hz, 3 H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.0, 156.7, 145.6, 139.2, 136.9, 135.4, 134.9, 128.4, 128.3, 126.8, 125.7, 123.9, 123.2, 123.0, 117.3, 116.8, 106.8, 92.8, 28.0, 27.9, 27.8, 23.3, 23.2, 22.3, 23.3. IR 3447, 3060, 2961, 2867, 1660, 1608, 1484, 1375, 1316, 1261, 1016 cm\(^{-1}\). HRMS (ESI) \( m/z \) calcd for C\(_{27}\)H\(_{31}\)N\(_2\)O (M+H\(^+\)) 399.2431, found 399.2438.
3-((2,6-diisopropylphenyl)imino)-2-(4-methoxyphenyl)-1-methylindolin-2-ol (4b)
Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J = 8.8$ Hz, 2 H), 7.28 (t, $J = 7.2$ Hz, 1 H), 7.15-7.08 (m, 3 H), 6.90 (d, $J = 8.8$ Hz, 2 H), 6.63 (d, $J = 8.4$ Hz, 1 H), 6.37 (t, $J = 7.6$ Hz, 1 H), 6.24 (d, $J = 7.6$ Hz, 1 H), 3.82 (s, 3 H), 3.50 (s, 1 H), 2.87-2.82 (m, 4 H), 2.36 (hept, $J = 6.8$ Hz, 1 H), 1.16 (d, $J = 7.2$ Hz, 3 H), 0.97 (d, $J = 6.8$ Hz, 3 H), 0.84 (d, $J = 6.8$ Hz, 3 H), 0.79 (d, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.2, 159.6, 156.6, 145.7, 136.9, 135.5, 134.9, 131.4, 126.8, 123.9, 123.2, 123.0, 117.2, 116.8, 113.7, 106.8, 92.7, 55.3, 28.0, 27.9, 27.9, 23.3, 23.3, 22.5. IR 3449, 3059, 2925, 2855, 1662, 1608, 1462, 1377, 1315, 1251, 1172 cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{28}$H$_{33}$N$_2$O$_2$ (M+H)$^+$ 429.2537, found 429.2542.

3-((2,6-diisopropylphenyl)imino)-2-(4-fluorophenyl)-1-methylindolin-2-ol (4c)
Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52-7.48 (m, 2 H), 7.30 (t, $J = 7.6$ Hz, 1 H), 7.18-7.14 (m, 1 H), 7.13-7.05 (m, 4 H), 6.60 (d, $J = 8.0$ Hz, 1 H), 6.40 (t, $J = 7.6$ Hz, 1 H), 6.28 (d, $J = 7.2$ Hz, 1 H), 3.59 (s, 1 H), 2.90-2.83 (m, 4 H), 2.32 (hept, $J = 6.8$ Hz, 1 H), 1.19 (d, $J = 6.8$ Hz, 3 H), 0.99 (d, $J = 6.8$ Hz, 3 H), 0.85 (d, $J = 7.2$ Hz, 3 H), 0.79 (d, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 162.7 (d, $J = 245.2$ Hz), 156.5, 145.5, 136.7, 135.3, 135.2 (d, $J = 3.0$ Hz), 135.0, 127.7 (d, $J = 8.2$ Hz), 126.8, 124.0, 123.2, 123.1, 117.4, 116.5, 115.2 (d, $J = 21.4$ Hz), 106.8, 92.4, 28.0, 27.9, 27.7, 23.2, 23.1, 22.3. IR 3439, 3062, 2962, 2869, 1660, 1608, 1483, 1374, 1316, 1226, 1157, 1016 cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{27}$H$_{30}$FN$_2$O (M+H)$^+$ 417.2337, found 417.2342.

3-((2,6-diisopropylphenyl)imino)-1-methyl-2-(4-(trifluoromethyl)phenyl)indolin-2-ol (4d)
Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 4 H), 7.32 (t, $J = 8.0$ Hz, 1 H), 7.18-7.09 (m, 3 H), 6.69 (d, $J = 8.4$ Hz, 1 H), 6.43 (t, $J = 7.6$ Hz, 1 H), 6.29 (d, $J = 7.6$ Hz, 1 H), 3.64 (s, 1 H), 2.88-2.83 (m, 4 H), 2.20 (hept, $J = 6.8$ Hz, 1 H), 1.19 (d, $J = 6.8$ Hz, 3 H), 1.00 (d, $J = 6.8$ Hz, 3 H), 0.81 (d, $J = 7.2$ Hz, 3 H), 0.72 (d, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 156.6, 145.4, 143.4, 136.6, 135.3, 135.1, 130.5 (q, $J = 32.2$ Hz), 126.9, 126.4, 125.4 (q, $J = 3.7$ Hz), 124.1, 124.1 (q, $J = 270.3$ Hz), 123.3, 123.1, 117.7, 116.5, 106.9, 92.4, 28.0, 27.9, 27.8, 23.2, 23.1, 23.0,
22.2. IR 3431, 3063, 2869, 1661, 1609, 1484, 1372, 1325, 1166, 1128, 1068 cm\(^{-1}\). HRMS (ESI) \(m/z\) calcd for \(C_{28}H_{30}F_3N_2O\) (M+H\(^+\)) 467.2305, found 467.2311.

3-((2,6-diisopropylphenyl)imino)-1-methyl-2-(4-tolyl)indolin-2-ol (4e)

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 8.0\) Hz, 2 H), 7.29 (t, \(J = 7.8\) Hz, 1 H), 7.20-7.10 (m, 5 H), 6.65 (d, \(J = 8.4\) Hz, 1 H), 6.39 (t, \(J = 7.6\) Hz, 1 H), 6.28 (d, \(J = 7.2\) Hz, 1 H), 3.54 (s, 1 H), 2.93-2.84 (m, 4 H), 2.40-2.33 (m, 4 H), 1.19 (d, \(J = 6.8\) Hz, 3 H), 1.00 (d, \(J = 6.8\) Hz, 3 H), 0.86 (d, \(J = 6.8\) Hz, 3 H), 0.79 (d, \(J = 7.2\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.1, 156.7, 145.7, 138.0, 136.8, 136.3, 135.4, 134.8, 129.0, 126.8, 125.7, 123.8, 123.2, 123.0, 117.2, 116.8, 106.7, 92.8, 27.9, 27.8, 23.2, 23.2, 22.4, 21.1. IR 3432, 3058, 2960, 2867, 1660, 1608, 1484, 1375, 1315, 1015 cm\(^{-1}\). HRMS (ESI) \(m/z\) calcd for \(C_{28}H_{33}N_2O\) (M+H\(^+\)) 413.2587, found 413.2593.

2-(4-(tert-butyl)phenyl)-3-((2,6-diisopropylphenyl)imino)-1-methylindolin-2-ol (4f)

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43-7.39 (m, 4 H), 7.29 (t, \(J = 7.8\) Hz, 1 H), 7.16-7.07 (m, 3 H), 6.66 (d, \(J = 8.0\) Hz, 1 H), 6.38 (t, \(J = 7.6\) Hz, 1 H), 6.27 (d, \(J = 7.6\) Hz, 1 H), 3.58 (s, 1 H), 2.91-2.84 (m, 4 H), 2.24 (hept, \(J = 6.8\) Hz, 1 H), 1.34 (s, 9 H), 1.19 (d, \(J = 6.8\) Hz, 3 H), 0.99 (d, \(J = 6.8\) Hz, 3 H), 0.79 (d, \(J = 6.8\) Hz, 3 H), 0.73 (d, \(J = 6.8\) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.9, 156.7, 151.1, 145.6, 136.9, 136.1, 135.4, 134.8, 126.8, 125.4, 125.3, 123.8, 123.1, 123.0, 117.1, 116.7, 106.6, 92.8, 34.5, 31.3, 31.3, 31.3, 27.9, 27.9, 27.7, 23.3, 23.3, 23.2, 22.4. IR 3435, 3060, 2960, 2866, 1672, 1609, 1484, 1379, 1315, 1013 cm\(^{-1}\). HRMS (ESI) \(m/z\) calcd for \(C_{31}H_{39}N_2O\) (M+H\(^+\)) 455.3057, found 455.3063.
2-(4-chlorophenyl)-3-((2,6-diisopropylphenyl)imino)-1-methylindolin-2-ol (4g)

Yellow solid. m.p.: 57-58 °C. 1H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.4 Hz, 2 H), 7.35 (d, J = 8.4 Hz, 2 H), 7.30 (t, J = 8.0 Hz, 1 H), 7.17-7.11 (m, 3 H), 6.65 (d, J = 8.4 Hz, 1 H), 6.40 (t, J = 7.6 Hz, 1 H), 6.27 (d, J = 7.6 Hz, 1 H), 3.57 (s, 1 H), 3.58 (s, 1 H), 2.89-2.85 (m, 4 H), 2.31 (hept, J = 6.8 Hz, 1 H), 1.81 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.85 (d, J = 6.8 Hz, 3 H), 0.79 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl₃) δ 170.6, 156.5, 145.5, 137.9, 136.6, 135.3, 135.0, 134.2, 128.5, 127.4, 126.8, 124.0, 123.1, 117.5, 116.6, 106.9, 92.4, 28.0, 27.9, 27.8, 23.2, 23.1, 23.1, 22.3. IR 3432, 3060, 2960, 2867, 1660, 1608, 1485, 1372, 1316, 1091, 1014 cm⁻¹. HRMS (ESI) m/z calcd for C_{27}H_{30}ClN₂O (M+H)⁺ 433.2041, found 433.2047.

2-(4-bromophenyl)-3-((2,6-diisopropylphenyl)imino)-1-methylindolin-2-ol (4h)

Yellow solid. m.p.: 59-60 °C. 1H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.8 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 1 H), 7.17-7.10 (m, 3 H), 6.65 (d, J = 8.0 Hz, 1 H), 6.40 (t, J = 7.6 Hz, 1 H), 6.27 (d, J = 7.6 Hz, 1 H), 3.57 (s, 1 H), 3.58 (s, 1 H), 2.89-2.82 (m, 4 H), 2.30 (hept, J = 6.8 Hz, 1 H), 1.81 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.85 (d, J = 6.8 Hz, 3 H), 0.79 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl₃) δ 170.6, 156.5, 145.4, 138.5, 136.6, 135.3, 135.0, 134.2, 128.5, 127.4, 126.8, 124.0, 123.2, 123.1, 122.4, 117.5, 116.5, 106.9, 92.4, 28.0, 27.9, 27.8, 23.2, 23.1, 23.1, 22.3. IR 3428, 3059, 2960, 2867, 1660, 1608, 1485, 1372, 1316, 1091, 1011 cm⁻¹. HRMS (ESI) m/z calcd for C_{27}H_{30}BrN₂O (M+H)⁺ 477.1536, found 477.1542.

2-(2-chlorophenyl)-3-((2,6-diisopropylphenyl)imino)-1-methylindolin-2-ol (4i)

Yellow solid. m.p.: 118-119 °C. 1H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.0 Hz, 1 H), 7.43-7.39 (m, 2 H), 7.35-7.27 (m, 2 H), 7.17-7.13 (m, 3 H), 6.63 (d, J = 8.0 Hz, 1 H), 6.43-6.36 (m, 2 H), 3.19 (s, 1 H), 2.96-2.85 (m, 2 H), 2.83 (s, 3 H), 1.81 (d, J = 7.2 Hz, 3 H), 1.04 (t, J = 6.8 Hz, 6 H), 0.88 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl₃) δ 170.9, 156.3, 145.5, 136.8, 136.8, 135.5, 134.6, 132.3, 130.4, 130.1, 129.8, 126.8, 126.2, 123.9, 123.2, 123.1, 117.5, 117.2, 107.3, 91.7, 27.9, 27.7, 27.4, 23.7, 23.2, 23.1, 22.8. IR 3449, 3054, 2958, 2866, 1669, 1655, 1611, 1485, 1376, 1317, 1157, 1008 cm⁻¹. HRMS (ESI) m/z calcd for C_{27}H_{30}ClN₂O (M+H)⁺ 433.2041, found 433.2045.
3-((2,6-diisopropylphenyl)imino)-1-methyl-2-(2-tolyl)indolin-2-ol (4j)

Yellow solid. m.p.: 102-103 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.2 Hz, 1 H), 7.33-7.25 (m, 3 H), 7.20-7.11 (m, 4 H), 6.64 (d, J = 8.0 Hz, 1 H), 6.40 (t, J = 7.6 Hz, 1 H), 6.34 (d, J = 7.6 Hz, 1 H), 3.10 (s, 1 H), 2.90 (hept, J = 6.8 Hz, 1 H), 2.83 (s, 3 H), 2.57 (hept, J = 6.8 Hz, 1 H), 2.13 (s, 3 H), 1.17 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.86 (d, J = 6.8 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 155.9, 145.7, 137.3, 136.5, 136.0, 135.4, 134.9, 131.5, 128.5, 127.9, 126.4, 125.9, 123.9, 123.2, 123.1, 117.2, 117.1, 107.3, 92.6, 27.9, 27.8, 27.2, 23.9, 23.2, 23.0, 22.7, 20.8. IR 3458, 3061, 2958, 2866, 1668, 1610, 1485, 1377, 1318, 1157, 1004 cm⁻¹. HRMS (ESI) m/z calcd for C₂₈H₃₃N₂O (M+H)⁺ 413.2587, found 413.2591.

3-((2,6-diisopropylphenyl)imino)-1-methyl-2-(3-tolyl)indolin-2-ol (4k)

Yellow solid. m.p.: 45-46 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (s, 1 H), 7.31-7.23 (m, 3 H), 7.16-7.10 (m, 4 H), 6.65 (d, J = 8.0 Hz, 1 H), 6.38 (t, J = 7.2 Hz, 1 H), 6.26 (d, J = 7.6 Hz, 1 H), 3.49 (s, 1 H), 2.91-2.83 (m, 4 H), 2.41-2.34 (m, 4 H), 1.17 (d, J = 6.8 Hz, 3 H), 0.98 (d, J = 6.8 Hz, 3 H), 0.86 (d, J = 6.8 Hz, 3 H), 0.79 (d, J = 6.8 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 155.7, 145.7, 139.2, 138.1, 136.9, 135.4, 134.8, 129.0, 128.2, 126.8, 126.3, 123.9, 123.2, 123.0, 122.7, 117.2, 116.8, 106.8, 92.7, 27.9, 27.9, 27.8, 23.3, 23.3, 23.2, 22.4, 21.5. IR 3428, 3059, 2960, 2867, 1660, 1608, 1484, 1375, 1316, 1157, 1008 cm⁻¹. HRMS (ESI) m/z calcd for C₂₈H₃₃N₂O (M+H)⁺ 413.2587, found 413.2591.

3-((2,6-diisopropylphenyl)imino)-1-methyl-2-(naphthalen-1-yl)indolin-2-ol (4l)

Yellow solid. m.p.: 79-80 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 7.2 Hz, 1 H),
7.90 (t, J = 7.2 Hz, 2 H), 7.60 (t, J = 7.6 Hz, 2 H), 7.46 (t, J = 7.6 Hz, 1 H), 7.39 (t, J = 7.6 Hz, 1 H), 7.29 (t, J = 7.2 Hz, 1 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.09 (t, J = 7.6 Hz, 1 H), 7.04 (d, J = 7.2 Hz, 1 H), 6.75 (d, J = 8.4 Hz, 1 H), 6.52 (t, J = 7.6 Hz, 1 H), 6.45 (d, J = 7.6 Hz, 1 H), 3.15 (s, 1 H), 2.96 (hept, J = 6.8 Hz, 1 H), 2.82 (s, 3 H), 2.26 (hept, J = 6.8 Hz, 1 H), 1.19 (d, J = 6.8 Hz, 3 H), 1.06 (d, J = 6.8 Hz, 3 H), 0.87 (d, J = 7.2 Hz, 3 H), 0.29 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl3) δ 171.5, 156.0, 145.7, 136.4, 135.4, 134.6, 134.1, 130.5, 129.9, 128.8, 127.0, 126.6, 125.9, 125.3, 125.0, 124.7, 123.9, 123.1, 117.8, 117.1, 108.1, 92.5, 28.0, 27.4, 23.4, 23.2, 23.0, 22.1. IR 3440, 3054, 2959, 2866, 1661, 1608, 1482, 1361, 1316, 1160, 1000 cm⁻¹. HRMS (ESI) m/z calcd for C31H33N2O (M+H)+ 449.2587, found 449.2582.

3-((2,6-diethylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4m)
Yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.50 (d, J = 7.8 Hz, 2 H), 7.40-7.28 (m, 4 H), 7.08 (d, J = 6.8 Hz, 1 H), 7.05-7.01 (m, 2 H), 6.65 (d, J = 8.0 Hz, 1 H), 6.40 (t, J = 7.2 Hz, 1 H), 6.30 (d, J = 7.2 Hz, 1 H), 3.46 (s, 1 H), 2.86 (s, 3 H), 2.53-2.43 (m, 1 H), 2.38-2.28 (m, 1 H), 2.04-1.93 (m, 2 H), 1.09 (t, J = 7.6 Hz, 3 H), 0.65 (t, J = 7.6 Hz, 3 H). 13C NMR (100 MHz, CDCl3) δ 170.8, 156.6, 146.8, 139.3, 134.9, 132.3, 130.8, 128.4, 128.3, 126.5, 126.0, 125.8, 125.8, 123.6, 117.5, 116.8, 106.7, 92.8, 27.9, 24.6, 24.1, 13.8, 13.7. IR 3433, 3060, 2964, 2872, 2872, 1662, 1608, 1484, 1448, 1373, 1316, 1162, 1015 cm⁻¹. HRMS (ESI) m/z calcd for C25H27N2O (M+H)+ 371.2118, found 371.2121.

3-((2,6-diisopropylphenyl)imino)-1-ethyl-2-phenylindolin-2-ol (4n)
Yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 8.0 Hz, 2 H), 7.39-7.33 (m, 3 H), 7.28 (t, J = 7.6 Hz, 1 H), 7.16-7.08 (m, 3 H), 6.70 (d, J = 8.0 Hz, 1 H), 6.36 (t, J = 8.0 Hz, 1 H), 6.27 (d, J = 7.6 Hz, 1 H), 3.47-3.38 (m, 2 H), 3.32-3.22 (m, 1 H), 2.86 (hept, J = 6.8 Hz, 1 H), 2.31 (hept, J = 6.8 Hz, 1 H), 1.20-1.16 (m, 6 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.84 (d, J = 6.8 Hz, 3 H), 0.74 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl3) δ 171.5, 156.2, 145.6, 140.2, 136.9, 135.4, 134.8, 128.3, 128.2, 127.0, 125.9, 123.8, 123.2, 123.0, 116.9, 116.5, 106.8, 93.0, 37.3, 27.9, 27.8, 23.3, 23.3, 23.2, 22.4, 14.2. IR 3432, 3060, 2962, 2868, 1660, 1607, 1482, 1447, 1353, 1330, 1163, 1022.
3-((2,6-diisopropylphenyl)imino)-1,5-dimethyl-2-phenylindolin-2-ol (4o)
Yellow solid. m.p.: 137-138 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.8 Hz, 2 H), 7.39-7.33 (m, 3 H), 7.15-7.06 (m, 4 H), 6.57 (d, J = 8.4 Hz, 1 H), 6.05 (s, 1 H), 3.54 (s, 1 H), 2.89-2.80 (m, 4 H), 2.30 (hept, J = 6.8 Hz, 1 H), 1.98 (s, 3 H), 1.17 (d, J = 6.8 Hz, 3 H), 0.81 (d, J = 6.8 Hz, 3 H), 0.75 (d, J = 6.8 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 155.1, 145.6, 139.4, 136.9, 135.7, 135.4, 128.3, 128.2, 126.9, 126.3, 125.7, 123.9, 123.2, 123.0, 116.9, 106.6, 93.1, 28.1, 27.9, 27.8, 23.3, 23.2, 23.1, 22.3, 20.5. IR 3492, 3061, 2960, 2863, 1661, 1618, 1500, 1431, 1374, 1286, 1019 cm⁻¹. HRMS (ESI) m/z calcd for C₂₈H₃₃N₂O (M+H)⁺ 413.2587, found 413.2593.

5-bromo-3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4p)
Yellow solid. m.p.: 49-51 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 7.2 Hz, 2 H), 7.41-7.35 (m, 4 H), 7.18-7.08 (m, 3 H), 6.54 (d, J = 8.4 Hz, 1 H), 6.30 (s, 1 H), 3.55 (s, 1 H), 2.84-2.78 (m, 4 H), 2.25 (hept, J = 6.8 Hz, 1 H), 1.17 (d, J = 6.8 Hz, 3 H), 1.01 (d, J = 6.8 Hz, 3 H), 0.82 (d, J = 6.8 Hz, 3 H), 0.74 (d, J = 6.8 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 155.4, 145.0, 145.0, 138.8, 137.2, 136.5, 135.0, 129.1, 128.5, 128.5, 125.6, 124.4, 123.4, 123.2, 118.2, 108.2, 108.2, 93.0, 28.0, 27.9, 27.9, 23.3, 23.1, 23.1, 22.3. IR 3434, 3061, 2960, 2867, 1661, 1601, 1480, 1373, 1272, 1084, 1019 cm⁻¹. HRMS (ESI) m/z calcd for C₂₇H₃₀BrN₂O (M+H)⁺ 477.1536, found 477.1542.

3-((2,6-diisopropylphenyl)imino)-1,6-dimethyl-2-phenylindolin-2-ol (4q)
Yellow solid. m.p.: 84-85 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.8 Hz, 2 H),
7.40-7.34 (m, 3 H), 7.16-7.07 (m, 3 H), 6.47 (s, 1 H), 6.22 (d, \( J = 7.6 \) Hz, 1 H), 6.15 (d, \( J = 8.0 \) Hz, 1 H), 3.56 (s, 1 H), 2.92-2.86 (m, 4 H), 2.34-2.28 (m, 4 H), 1.18 (d, \( J = 7.2 \) Hz, 3 H), 0.99 (d, \( J = 6.8 \) Hz, 3 H), 0.83 (d, \( J = 6.8 \) Hz, 3 H), 0.74 (d, \( J = 6.8 \) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.7, 157.0, 146.1, 145.8, 139.4, 137.0, 135.6, 128.3, 128.2, 126.6, 125.7, 123.7, 123.1, 123.0, 118.6, 114.5, 107.2, 93.1, 27.9, 27.8, 23.2, 23.2, 22.4, 22.3. IR 3358, 3060, 2960, 2866, 1652, 1616, 1487, 1447, 1381, 1315, 1022 cm\(^{-1}\). HRMS (ESI) \( m/z \) calcd for C\(_{28}\)H\(_{33}\)N\(_2\)O (M+H)\(^+\) 413.2587, found 413.2591.

![Image of 6-chloro-3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4r)](image)

6-chloro-3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4r)
Yellow solid. m.p.: 52-53 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.47 (d, \( J = 8.0 \) Hz, 2 H), 7.41-7.35 (m, 3 H), 7.15-7.06 (m, 3 H), 6.63 (s, 1 H), 6.34 (d, \( J = 8.4 \) Hz, 1 H), 6.13 (d, \( J = 8.4 \) Hz, 1 H), 3.54 (s, 1 H), 2.86-2.79 (m, 4 H), 2.25 (hept, \( J = 6.8 \) Hz, 1 H), 1.17 (d, \( J = 6.8 \) Hz, 3 H), 0.98 (d, \( J = 6.8 \) Hz, 3 H), 0.80 (d, \( J = 6.8 \) Hz, 3 H), 0.73 (d, \( J = 6.8 \) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 169.7, 157.3, 145.4, 141.2, 138.8, 136.7, 135.3, 128.5, 128.5, 127.5, 125.6, 124.1, 123.3, 123.1, 117.5, 115.2, 107.0, 93.2, 28.0, 27.8, 27.8, 23.2, 23.2, 22.3. IR 3431, 3060, 2960, 2866, 1662, 1602, 1482, 1416, 1361, 1306, 1064, 1016 cm\(^{-1}\). HRMS (ESI) \( m/z \) calcd for C\(_{27}\)H\(_{30}\)ClN\(_2\)O (M+H)\(^+\) 433.2041, found 433.2047.

![Image of 7-chloro-3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4s)](image)

7-chloro-3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4s)
Yellow solid. m.p.: 57-58 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.56 (d, \( J = 6.8 \) Hz, 2 H), 7.42-7.36 (m, 3 H), 7.22 (d, \( J = 8.0 \) Hz, 1 H), 7.16-7.09 (m, 3 H), 6.29 (t, \( J = 8.0 \) Hz, 1 H), 6.22 (d, \( J = 8.0 \) Hz, 1 H), 3.60 (s, 1 H), 3.30 (s, 3 H), 2.83 (hept, \( J = 6.8 \) Hz, 1 H), 2.22 (hept, \( J = 6.8 \) Hz, 1 H), 1.19 (d, \( J = 6.8 \) Hz, 3 H), 0.99 (d, \( J = 6.8 \) Hz, 3 H), 0.80 (d, \( J = 6.8 \) Hz, 3 H), 0.73 (d, \( J = 6.8 \) Hz, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 169.5, 151.7, 145.2, 139.0, 136.7, 136.5, 135.0, 128.5, 125.8, 125.4, 124.0, 123.3, 123.1, 119.6, 118.1, 114.1, 93.2, 31.0, 28.0, 27.8, 23.2, 23.2, 22.3. IR 3439, 3060, 2960, 2866, 1664, 1598, 1482, 1412, 1360, 1270, 1129, 1021 cm\(^{-1}\). HRMS (ESI) \( m/z \) calcd for C\(_{27}\)H\(_{30}\)ClN\(_2\)O (M+H)\(^+\) 433.2041, found 433.2046.
5,7-dichloro-3-((2,6-diisopropylphenyl)imino)-1-methyl-2-phenylindolin-2-ol (4t)
Yellow solid. m.p.: 48-49 °C. 1H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 6.8 Hz, 2 H), 7.42-7.35 (m, 3 H), 7.22 (s, 1 H), 7.16-7.06 (m, 3 H), 6.09 (s, 1 H), 3.56 (s, 1 H), 3.26 (s, 3 H), 2.75 (hept, J = 6.8 Hz, 1 H), 2.15 (hept, J = 6.8 Hz, 1 H), 1.16 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 0.78 (d, J = 6.8 Hz, 3 H), 0.71 (d, J = 6.8 Hz, 3 H). 13C NMR (100 MHz, CDCl₃) δ 168.4, 150.4, 144.7, 138.6, 136.2, 135.8, 134.7, 128.7, 128.6, 125.7, 124.9, 124.5, 123.5, 123.3, 121.8, 120.0, 114.5, 93.6, 30.9, 28.1, 27.9, 23.2, 23.0, 22.3. IR 3438, 3063, 2961, 2867, 1666, 1597, 1556, 1473, 1404, 1344, 1245, 1165, 1059 cm⁻¹. HRMS (ESI) m/z calcd for C₂₇H₂₉Cl₂N₂O (M+H)⁺ 467.1651, found 467.1658.

2,6-diisopropyl-N-(2-phenyl-3H-indol-3-ylidene)aniline (5a)
Red solid. m.p.: 111-112 °C. 1H NMR (400 MHz, CDCl₃) δ 8.60 (d, J = 6.4 Hz, 2 H), 7.52-7.46 (m, 4 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.26-7.21 (m, 3 H), 6.86 (t, J = 7.2 Hz, 1 H), 6.25 (d, J = 7.2 Hz, 1 H), 2.76 (hept, J = 6.8 Hz, 2 H), 1.16 (d, J = 6.8 Hz, 6 H), 0.96 (d, J = 6.8 Hz, 6 H). 13C NMR (100 MHz, CDCl₃) δ 165.5, 165.5, 157.2, 146.5, 134.1, 134.1, 133.2, 132.3, 131.1, 130.0, 130.0, 128.4, 128.4, 127.1, 125.4, 125.0, 123.5, 123.5, 122.1, 121.3, 28.5, 28.5, 23.2, 23.2, 23.0, 23.0. IR 3438, 3063, 2961, 2867, 1666, 1597, 1556, 1473, 1404, 1344, 1245, 1165, 1059 cm⁻¹. HRMS (ESI) m/z calcd for C₂₆H₂₇N₂ (M+H)⁺ 367.2169, found 367.2170.

2,6-diisopropyl-N-(2-(4-tolyl)-3H-indol-3-ylidene)aniline (5b)
Red solid. m.p.: 126-127 °C. 1H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 8.0 Hz, 2 H), 7.46 (d, J = 7.6 Hz, 1 H), 7.33-7.30 (m, 3 H), 7.25-7.22 (m, 3 H), 6.85 (t, J = 7.2 Hz, 1 H), 6.24 (d, J = 7.6 Hz, 1 H), 2.77 (hept, J = 6.8 Hz, 2 H), 2.43 (s, 3 H), 1.16 (d, J =
6.8 Hz, 6 H), 0.96 (d, J = 6.8 Hz, 6 H). $^1$H NMR (100 MHz, CDCl$_3$) $\delta$ 165.6, 165.3, 157.4, 146.5, 141.6, 134.1, 134.1, 133.2, 129.9, 129.9, 129.6, 129.2, 129.2, 126.9, 125.3, 124.9, 123.4, 123.4, 122.2, 121.1, 28.5, 28.5, 23.1, 23.1, 22.9, 22.9, 21.6. IR 3068, 2961, 2866, 1649, 1605, 1504, 1430, 1360 cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{27}$H$_{29}$N$_2$ (M+H)$^+$ 381.2325, found 381.2322.

N-(2-(4-(tert-butyl)phenyl)-3H-indol-3-ylidene)-2,6-diisopropylaniline (5c)
Red solid. m.p.: 97-98 $^\circ$C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.58 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 7.6 Hz, 1 H), 7.31 (t, J = 7.6 Hz, 1 H), 7.26-7.21 (m, 3 H), 6.84 (t, J = 7.6 Hz, 1 H), 6.22 (d, J = 7.2 Hz, 1 H), 2.78 (hept, J = 6.8 Hz, 2 H), 1.38 (s, 9 H), 1.16 (d, J = 6.8 Hz, 6 H), 0.95 (d, J = 6.8 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 165.2, 157.4, 154.6, 146.5, 134.1, 134.1, 133.2, 129.8, 129.6, 126.9, 125.5, 125.5, 125.3, 124.9, 123.4, 123.4, 122.2, 121.1, 35.0, 31.1, 31.1, 28.5, 28.5, 23.2, 23.2, 23.0, 23.0. IR 3063, 2963, 2868, 1647, 1602, 1501, 1450, 1362, 1267 cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{30}$H$_{35}$N$_2$ (M+H)$^+$ 423.2795, found 423.2790.

N-(2-(4-chlorophenyl)-3H-indol-3-ylidene)-2,6-diisopropylaniline (5d)
Red solid. m.p.: 117-118 $^\circ$C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (d, J = 8.8 Hz, 2 H), 7.48-7.45 (m, 3 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.26-7.21 (m, 3 H), 6.87 (t, J = 7.2 Hz, 1 H), 6.25 (d, J = 7.6 Hz, 1 H), 2.73 (hept, J = 6.8 Hz, 2 H), 1.15 (d, J = 7.2 Hz, 6 H), 0.95 (d, J = 6.8 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.3, 164.3, 157.0, 146.3, 137.6, 134.0, 134.0, 133.4, 131.2, 131.2, 130.7, 128.8, 128.8, 127.3, 125.4, 125.1, 123.5, 123.5, 122.0, 121.4, 28.5, 28.5, 23.1, 23.1, 22.9, 22.9. IR 3070, 2961, 2865, 1633, 1590, 1488, 1450, 1357, 1269 cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{28}$H$_{26}$ClN$_2$ (M+H)$^+$ 401.1779, found 401.1782.
2,6-diisopropyl-N-(2-(3-tolyl)-3H-indol-3-ylidene)aniline (5e)

Red solid. m.p.: 146-147 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.44 (d, \( J = 7.6 \) Hz, 1 H), 8.39 (s, 1 H), 7.49 (d, \( J = 7.6 \) Hz, 1 H), 7.42 (t, \( J = 7.6 \) Hz, 1 H), 7.35 (t, \( J = 8.0 \) Hz, 2 H), 7.28-7.23 (m, 3 H), 6.89 (t, \( J = 7.2 \) Hz, 1 H), 6.28 (d, \( J = 7.2 \) Hz, 1 H), 2.79 (hept, \( J = 6.8 \) Hz, 2 H), 2.47 (s, 3 H), 1.18 (d, \( J = 6.8 \) Hz, 6 H), 0.98 (d, \( J = 6.8 \) Hz, 6 H).

\( ^13C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 165.7, 165.4, 157.2, 146.5, 138.1, 134.1, 134.1, 133.2, 132.2, 132.0, 130.3, 128.3, 127.5, 127.1, 125.3, 124.9, 123.4, 122.4, 121.2, 28.5, 28.5, 23.2, 23.2, 22.9, 22.9, 21.5. IR 3070, 2959, 2867, 1639, 1607, 1525, 1432, 1359, 1270 cm\(^{-1}\). HRMS (ESI) \( m/z \) calcd for C\(_{27}\)H\(_{29}\)N\(_2\) (M+H)\(^+\) 381.2325, found 381.2329.

1-(3-((2,6-diisopropylphenyl)imino)-2-phenylindolin-2-yl)propan-2-one (6a)

Yellow solid. m.p.: 184-185 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.55 (d, \( J = 7.6 \) Hz, 2 H), 7.31 (t, \( J = 7.2 \) Hz, 2 H), 7.26-7.19 (m, 2 H), 7.13 (d, \( J = 7.2 \) Hz, 1 H), 7.08-7.02 (m, 2 H), 6.83 (d, \( J = 8.0 \) Hz, 1 H), 6.35 (t, \( J = 7.6 \) Hz, 1 H), 6.15 (d, \( J = 8.0 \) Hz, 1 H), 5.90 (s, 1 H), 4.19 (d, \( J = 17.8 \) Hz, 1 H), 3.01 (d, \( J = 17.8 \) Hz, 1 H), 2.90 (hept, \( J = \)
6.8 Hz, 1 H), 2.23 (s, 3 H), 2.07 (hept, J = 6.8 Hz, 1 H), 1.24 (d, J = 6.8 Hz, 3 H), 0.98 (d, J = 6.8 Hz, 3 H), 0.71 (d, J = 6.8 Hz, 3 H), 0.56 (d, J = 6.8 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.4, 170.6, 156.3, 146.4, 141.4, 136.8, 135.5, 134.1, 128.4, 128.4, 127.1, 127.1, 125.2, 125.2, 123.4, 123.1, 122.9, 118.0, 117.5, 110.4, 68.3, 50.8, 31.4, 28.2, 27.5, 23.2, 23.1, 22.8, 22.7. IR 3059, 2959, 2865, 1715, 1648, 1602, 1482, 1360, 1318 cm$^{-1}$. HRMS (ESI) m/z calcd for C$_{29}$H$_{33}$N$_2$O (M+H)$^+$ 425.2587, found 425.2595.

6. References.

7. Copies of $^1$H and $^{13}$C NMR Spectra.

![NMR Spectra Image]

![NMR Spectra Image]