

Supporting Information

Rh(III)-catalyzed direct C-7 amination of indolines with anthranils

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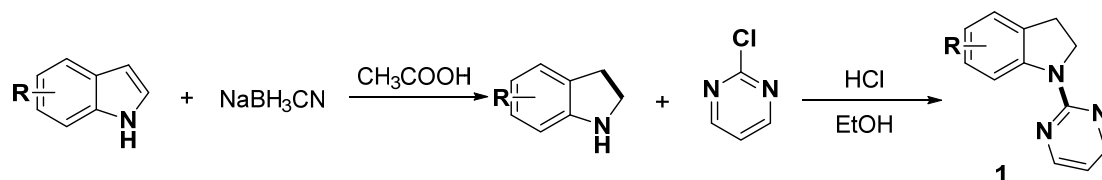
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General experimental procedures

All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a NMR spectrometer with CDCl_3 as solvent. Chemical shifts of ^1H and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl_3 : $\delta \text{H} = 7.26$ ppm, $\delta \text{C} = 77.16$ ppm). All coupling constants (J values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200–300 mesh.

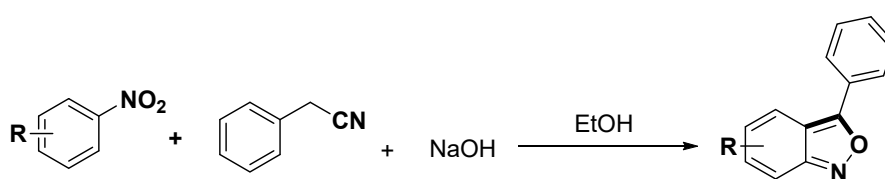
General Procedure for Synthesis of 1-(pyrimidin-2-yl) indoline derivatives (1) : To a solution of an indole (5.0 mmol, 1.0 equiv) in AcOH (25 mL) at 0°C was added NaBH_3CN (1.26 g, 20.0 mmol, 4 equiv) in portions. The reaction was allowed to stir at room temperature for 4 hours. 280 mL 50% NaOH saturated solution was then added slowly at 0°C and the reaction mixture was extracted with ethyl acetate three times. The combined organic layers were washed by water and sodium chloride saturated solution then were dried over MgSO_4 filtered. Then concentrated under reduced pressure. Indoline was purified through column chromatography on silica gel, and elution with petroleum ether/ ethyl acetate (20:1) gave the indoline in 85% yield.



The indoline and 2-chloropyrimidine (5 mmol, 1.2 equiv) was dissolved in a mixture of EtOH (50 mL). Concentrated hydrochloric acid (1 mL) was added to the mixture. Then, the resulting solution was refluxed overnight. EtOH was then removed under reduced pressure, and the aqueous phase was extracted twice with DCM. The combined organic layers were dried over MgSO_4 , filtered, and evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/ ethyl acetate (5:1) gave the product in 70% yield.

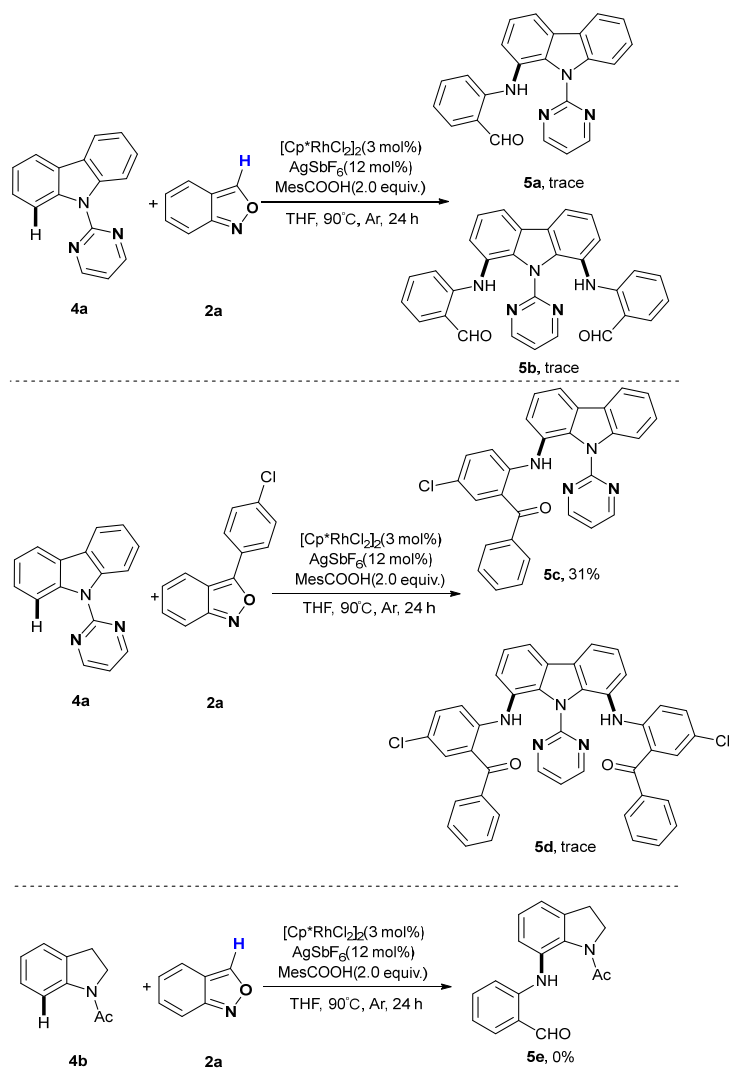
General Procedure for Synthesis of anthranils (2a-2f, 2m): To a solution of 2-nitrobenzaldehyde (10.0 mmol, 1.0 equiv) in a 1:1 mixture of EtOAc - MeOH (50 mL) at 25°C was added $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ (30.0 mmol, 3.0 equiv). The reaction was allowed to stir at 25°C for 20h. The reaction was partitioned between EtOAc (50 mL) and NaHCO_3 (50 mL). The aqueous phase was extracted with EtOAc (3 \times 20 mL) and the organic portions combined, washed with H_2O (20 mL), saturated aqueous NaCl (20 mL), dried over MgSO_4 , filtered and reduced *in vacuo*. The residue was purified by flash column chromatography on silica gel with petroleum ether/ ethyl acetate (20:1) to provide the title compound.

General Procedure for Synthesis of anthranils (2h-2l) :

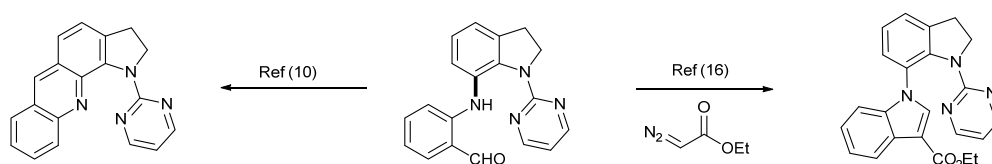


To a solution of NaOH (4.0 g) in EtOH (40 mL) refluxed for 0.5h, then added nitrobenzene (11.0 mmol) when cooled to 40°C, the mixture was allowed stirred at 40°C for 0.5h. Then the solution was cooled to room temperature, added 2-phenylacetonitrile (10.0 mmol) slowly, the mixture was stirred at room temperature for 3h. The residue was purified by flash column chromatography on silica gel with petroleum ether/ ethyl acetate (100:1) to provide the title compound.

Reactions of carbazole and N-acetyl indoline with anthranils:



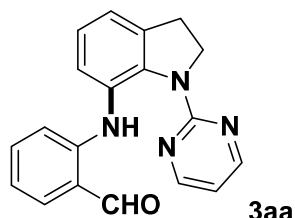
Potential synthetic applications of Rh(III)-catalyzed direct C-7 amination:



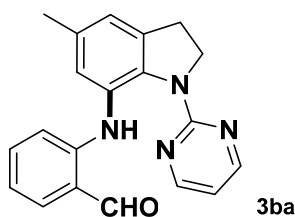
Representative procedures for the synthesis of product 3: Substituted 1-(pyrimidin-2-yl) indolines (0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (0.006 mmol), AgSbF_6 (0.024 mmol), anthranils (0.5 mmol) and MesCOOH (0.4 mmol) was dissolved in THF (2 mL) in a pressure tube. The mixture was stirred at 90°C for 24 h under argon atmosphere. After that, the solvent was removed under vacuum and

the residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate to afford product **3**.

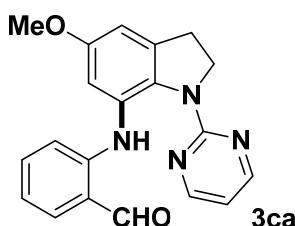
Characterization data of compounds **3**



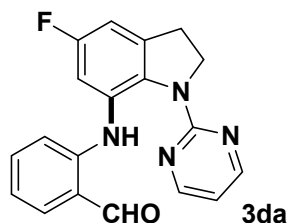
2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3aa) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 53 mg (84%). Yellow solid. M.P. 212-214°C. ^1H NMR (CDCl_3 , 400 MHz) δ 10.19 (s, 1H), 9.79 (s, 1H), 8.59 (m, 2H), 7.44 (d, $J = 7.7$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.21 (t, $J = 7.8$ Hz, 1H), 7.06 (m, 2H), 6.92 (d, $J = 8.6$ Hz, 1H), 6.72 (m, 2H), 4.44 (t, $J = 7.8$ Hz, 2H), 3.12 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.0, 160.6, 158.4, 147.8, 138.1, 136.8, 136.5, 135.1, 130.1, 125.0, 124.4, 121.2, 120.4, 116.7, 114.0, 112.2, 52.3, 29.6. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}$ 317.1402, found 317.1405.



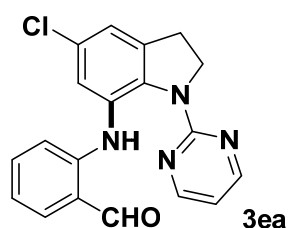
2-((5-methyl-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ba): Eluent: petroleum ether/ ethyl acetate (10:1). Yield 49 mg (75%). Yellow solid. M.P. 228-230°C. ^1H NMR (CDCl_3 , 400 MHz) δ 10.18 (s, 1H), 9.79 (s, 1H), 8.58 (m, 2H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.11 (s, 1H), 6.95 (m, 1H), 6.90 (s, 1H), 6.71 (m, 2H), 4.42 (t, $J = 7.8$ Hz, 2H), 3.08 (t, $J = 7.8$ Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.0, 160.7, 158.5, 147.9, 136.9, 136.6, 135.7, 135.1, 134.5, 129.7, 125.2, 122.1, 120.4, 116.6, 114.1, 112.0, 52.4, 29.6, 21.0. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}$ 331.1553, found 331.1550.



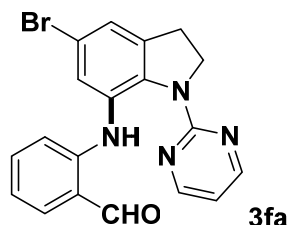
2-((5-methoxy-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ca) : Eluent: petroleum ether/ ethyl acetate (10:1). Yield 46 mg (67%). Yellow solid. M.P. 187-189 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 10.23 (s, 1H), 9.81 (s, 1H), 8.59 (m, 2H), 7.46 (m, 1H), 7.25 (m, 1H), 7.05 (d, $J = 8.6$ Hz, 1H), 6.84 (m, 1H), 6.73 (m, 2H), 6.68 (m, 1H), 4.44 (t, $J = 7.8$ Hz, 2H), 3.76 (s, 3H), 3.08 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 193.1, 160.8, 158.6, 157.4, 147.5, 138.2, 136.7, 135.2, 131.7, 130.9, 120.8, 117.1, 114.4, 111.9, 109.2, 108.1, 56.1, 52.5, 30.2. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$ 347.1503, found 347.1502.



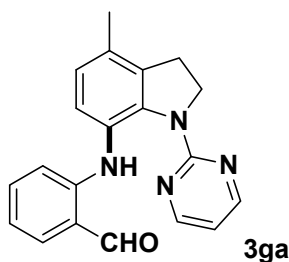
2-((5-fluoro-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3da) : Eluent: petroleum ether/ethyl acetate (10:1). Yield 41 mg (60%). Yellow solid. M.P. 143-145°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.19 (s, 1H), 9.81 (s, 1H), 8.62 (m, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.29 (m, 1H), 7.04 (m, 2H), 6.77 (m, 3H), 4.47 (t, *J* = 7.8 Hz, 2H), 3.10 (t, *J* = 7.7 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 193.1, 160.7, 160.0 (d, *J* = 242.4 Hz), 158.6, 146.8, 138.5 (d, *J* = 9.8 Hz), 136.6, 135.2, 134.1, 131.3 (d, *J* = 10.6 Hz), 121.1, 117.6, 114.4, 112.2, 110.4 (d, *J* = 24.5 Hz), 108.3 (d, *J* = 24.0 Hz), 52.6, 30.0. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₁₉H₁₅FN₄O 335.1303, found 335.1302.



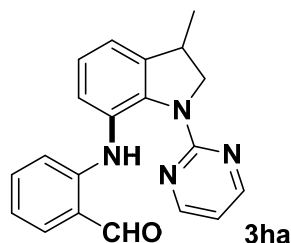
2-((5-chloro-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ea) : Eluent: petroleum ether/ethyl acetate (20:1). Yield 50 mg (72%). Yellow solid. M.P. 182-184°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.18 (s, 1H), 9.81 (s, 1H), 8.62 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 2H), 7.01 (m, 2H), 6.77 (m, 2H), 4.45 (t, *J* = 7.9 Hz, 2H), 3.10 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 193.1, 160.5, 158.6, 147.0, 138.5, 136.8, 136.6, 135.3, 131.1, 129.2, 124.2, 121.0, 121.0, 117.5, 114.3, 112.5, 52.4, 29.6. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₁₉H₁₅ClN₄O 351.1007, found 351.1006.



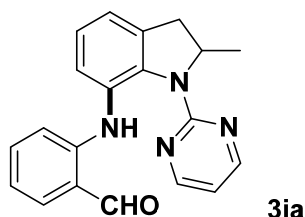
2-((5-bromo-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3fa) : Eluent: petroleum ether/ethyl acetate (5:1). Yield 58 mg (74%). Yellow solid. M.P. 183-185°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.18 (s, 1H), 9.80 (s, 1H), 8.61 (m, 2H), 7.47 (m, 1H), 7.43 (s, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.77 (m, 2H), 4.44 (t, *J* = 7.9 Hz, 2H), 3.10 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 193.1, 160.5, 158.5, 147.0, 138.8, 137.3, 136.6, 135.3, 131.5, 127.0, 123.9, 120.9, 117.5, 116.4, 114.2, 112.5, 52.4, 29.4. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₁₉H₁₅BrN₄O 395.0502, found 395.0504.



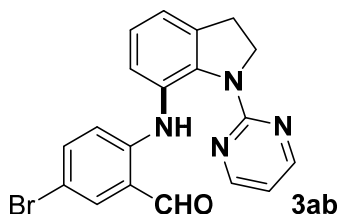
2-((4-methyl-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ga) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 50 mg (76%). Yellow solid. M.P. 195-197°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.11 (s, 1H), 9.78 (s, 1H), 8.58 (m, 2H), 7.42 (m, 1H), 7.20 (m, 2H), 6.89 (m, 2H), 6.73 (t, *J* = 4.8 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 4.44 (t, *J* = 7.9 Hz, 2H), 3.03 (t, *J* = 7.9 Hz, 2H), 2.28 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 193.1, 160.6, 158.4, 148.3, 137.9, 136.6, 135.1, 135.1, 130.8, 127.5, 125.6, 125.5, 120.2, 116.3, 113.8, 112.2, 52.1, 28.4, 18.6. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₀H₁₈N₄O 331.1553, found 331.1553.



2-((3-methyl-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ha) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 60 mg (91%). Yellow solid. M.P. 128-130°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.19 (s, 1H), 9.80 (s, 1H), 8.60 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (m, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.72 (m, 2H), 4.66 (m, 1H), 3.91 (m, 1H), 3.44 (h, *J* = 7.0 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 193.1, 160.7, 158.5, 147.8, 142.0, 137.8, 136.6, 135.1, 130.0, 124.9, 124.6, 120.5, 119.9, 116.8, 114.1, 112.1, 60.1, 36.1, 18.8. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₀H₁₈N₄O 331.1553, found 331.1557.

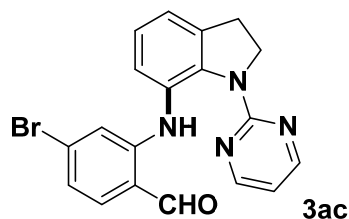


2-((2-methyl-1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ia) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 64 mg (97%). Yellow solid. M.P. 159-161°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.16 (s, 1H), 9.79 (s, 1H), 8.57 (m, 2H), 7.43 (d, *J* = 9.1 Hz, 1H), 7.28 (m, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 7.06 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.71 (m, 2H), 5.04 (p, *J* = 6.6 Hz, 1H), 3.48 (m, 1H), 2.56 (d, *J* = 15.6 Hz, 1H), 1.36 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 193.0, 160.1, 158.5, 148.0, 136.8, 136.5, 135.5, 135.0, 130.4, 125.2, 124.4, 121.8, 120.4, 116.6, 114.0, 112.2, 59.6, 36.8, 21.2. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₀H₁₈N₄O 331.1553, found 331.1552.

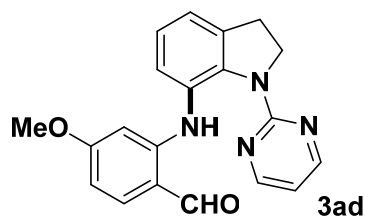


5-bromo-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ab) : Eluent: petroleum ether/ethyl acetate (10:1). Yield 65 mg (83%). Yellow solid. M.P. 211-213°C. ¹H NMR (CDCl₃, 400 MHz) δ 10.25 (s, 1H), 9.71 (s, 1H), 8.60 (m, 2H), 7.53 (s, 1H), 7.23 (m, 2H), 7.08 (m, 2H), 6.82 (d, *J* = 9.1 Hz, 1H), 6.75 (m, 1H), 4.45 (t, *J* = 7.7 Hz, 2H), 3.13 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz)

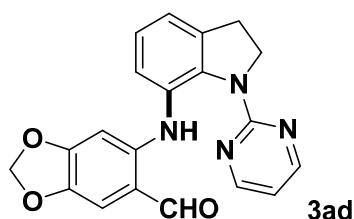
δ 191.8, 160.6, 158.6, 146.9, 138.3, 137.8, 137.1, 129.7, 126.8, 124.9, 124.7, 121.9, 121.7, 116.4, 112.4, 107.7, 52.4, 29.7. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{19}H_{15}BrN_4O$ 395.0502, found 395.0505.



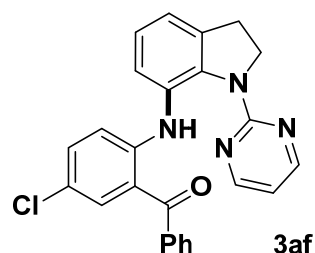
4-bromo-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ac) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 50 mg (64%). Yellow solid. M.P. 157-159°C. 1H NMR ($CDCl_3$, 400 MHz) δ 10.34 (s, 1H), 9.73(s, 1H), 8.60 (m, 2H), 7.27 (m, 2H), 7.10 (m, 2H), 7.05 (s, 1H), 6.81 (d, J = 8.2 Hz, 1H), 6.74 (t, J = 4.7 Hz, 1H), 4.45 (t, J = 7.8 Hz, 2H), 3.13 (t, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.8, 160.2, 158.1, 148.2, 138.0, 137.4, 136.7, 130.4, 128.8, 124.7, 124.4, 121.6, 119.5, 118.9, 116.2, 111.9, 51.9, 29.2. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{19}H_{15}BrN_4O$ 395.0502, found 395.0501.



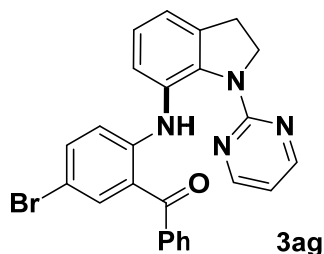
4-methoxy-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) benzaldehyde (3ad) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 53 mg (77%). Yellow solid. M.P. 132-134°C. 1H NMR ($CDCl_3$, 400 MHz) δ 10.26 (s, 1H), 9.63 (s, 1H), 8.59 (m, 2H), 7.33 (m, 2H), 7.06 (m, 2H), 6.73 (t, J = 4.8 Hz, 1H), 6.35 (m, 1H), 6.28 (m, 1H), 4.44 (t, J = 7.9 Hz, 2H), 3.69 (s, 3H), 3.13 (t, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1, 165.3, 160.6, 158.5, 150.0, 138.8, 138.3, 136.9, 129.8, 125.3, 124.4, 121.4, 115.4, 112.2, 104.7, 97.0, 55.4, 52.3, 29.6. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{20}H_{18}N_4O_2$ 347.1503, found 347.1500.



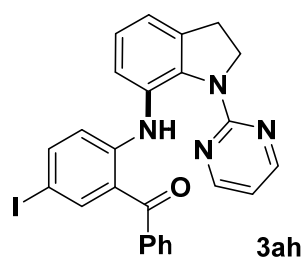
6-((1-(pyrimidin-2-yl) indolin-7-yl) amino) benzo[d][1,3]dioxole-5-carbaldehyde (3ad) : Eluent: petroleum ether/ ethyl acetate (5:1). Yield 45 mg (63%). Yellow solid. M.P. 120 - 122°C. 1H NMR ($CDCl_3$, 400 MHz) δ 10.36 (s, 1H), 9.55 (s, 1H), 8.58 (m, 2H), 7.23 (m, 1H), 7.06 (m, 2H), 6.80 (s, 1H), 6.73 (t, J = 4.8 Hz, 1H), 6.41 (s, 1H), 5.87 (s, 2H), 4.44 (t, J = 7.9 Hz, 2H), 3.12 (t, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.0, 160.7, 158.5, 154.1, 147.2, 139.6, 138.3, 136.9, 130.4, 125.1, 124.7, 121.4, 113.8, 112.4, 112.3, 101.6, 94.7, 52.4, 29.7. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{20}H_{16}N_4O_3$ 361.1295, found 361.1291.



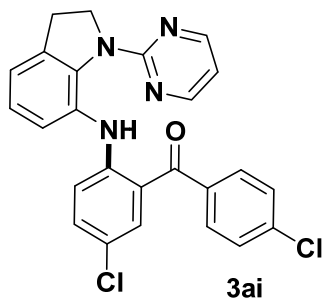
(5-chloro-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (phenyl) methanone (3af) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 72 mg (85%). Yellow solid. M.P. 144-146°C. ¹H NMR (CDCl₃, 400 MHz) δ 9.85 (s, 1H), 8.58 (m, 2H), 7.70 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.32 (m, 1H), 7.23 (m, 1H), 7.14 (m, 1H), 7.02 (m, 3H), 6.70 (t, *J* = 4.8 Hz, 1H), 4.46 (t, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 196.2, 160.4, 158.5, 146.1, 139.1, 137.3, 136.8, 133.1, 132.5, 132.0, 131.2, 129.7, 128.4, 124.6, 123.4, 123.1, 120.9, 120.4, 118.0, 112.0, 52.2, 29.5. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₅H₁₉ClN₄O 427.1320, found 427.1320.



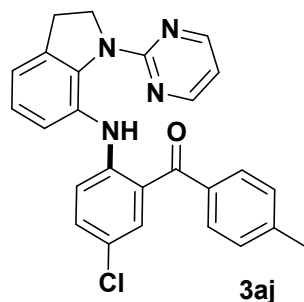
(5-bromo-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (phenyl) methanone (3ag) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 74 mg (80%). Yellow solid. M.P. 209-211°C. ¹H NMR (CDCl₃, 400 MHz) δ 9.86 (s, 1H), 8.57 (m, 2H), 7.70 (m, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (m, 3H), 7.25 (m, 2H), 7.03 (m, 2H), 6.95 (d, *J* = 9.1 Hz, 1H), 6.70 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 196.1, 160.3, 158.4, 146.5, 139.1, 137.3, 136.8, 135.8, 135.4, 131.9, 131.0, 129.7, 128.3, 124.5, 123.6, 123.4, 120.4, 118.2, 111.9, 107.7, 52.1, 29.5. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₅H₁₉BrN₄O 471.0820, found 471.0826.



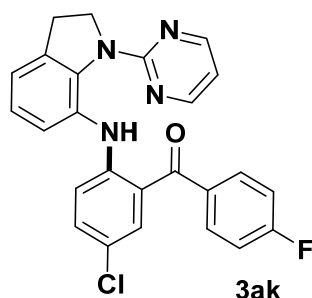
(5-iodo-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (phenyl) methanone (3ah) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 70 mg (68%). Yellow solid. M.P. 165-167°C. ¹H NMR (CDCl₃, 400 MHz) δ 9.86 (s, 1H), 8.57 (m, 2H), 7.70 (m, 2H), 7.61 (s, 1H), 7.55 (m, 1H), 7.45 (m, 3H), 7.23 (m, 1H), 7.03 (m, 2H), 6.84 (m, 1H), 6.70 (m, 1H), 4.45 (t, *J* = 7.8 Hz, 2H), 3.11 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 196.0, 160.3, 158.4, 147.0, 141.4, 141.4, 139.1, 137.4, 136.8, 132.0, 130.8, 129.7, 128.4, 124.5, 124.4, 123.5, 120.6, 118.6, 112.0, 76.5, 52.2, 29.5. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₅H₁₉I N₄O 519.0676, found 519.0676.



(5-chloro-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (4-chlorophenyl) methanone (3ai) : Eluent: petroleum ether/ ethyl acetate (10:1). Yield 48 mg (52%). Yellow solid. M.P. 208-210°C. ¹H NMR (CDCl₃, 400 MHz) δ 9.82 (s, 1H), 8.58 (m, 2H), 7.66 (s, 2H), 7.45(m, 2H), 7.27 (s, 1H), 7.21 (d, *J* = 6.3 Hz, 1H), 7.16 (m, 1H), 7.02 (m, 3H), 6.71 (t, *J* = 5.3 Hz, 1H), 4.46 (t, *J* = 7.9 Hz, 2H), 3.12 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 194.9, 160.3, 158.5, 146.2, 138.4, 137.4, 137.3, 136.9, 133.3, 132.2, 131.1, 131.0, 128.7, 124.6, 123.4, 122.7, 121.0, 120.5, 118.1, 112.0, 52.2, 29.5. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₅H₁₈Cl₂N₄O 461.0930, found 461.0930.

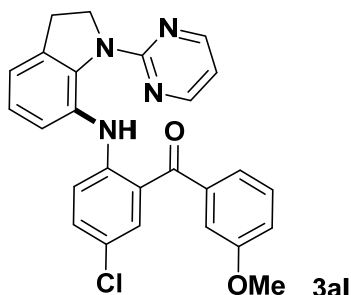


(5-chloro-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (p-tolyl) methanone (3aj) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 59 mg (67%). Yellow solid. M.P. 188-190°C. ¹H NMR (CDCl₃, 400 MHz) δ 9.70 (s, 1H), 8.56 (m, 2H), 7.64 (m, 2H), 7.32 (m, 1H), 7.24(m, 3H), 7.13(m, 1H), 7.02(m,3H), 6.69 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 2H), 3.10 (t, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 195.9, 160.3, 158.4, 145.7, 142.8, 137.1, 136.7, 136.2, 132.7, 132.2, 131.3, 130.0, 129.1, 124.5, 123.8, 123.1, 121.0, 120.2, 118.0, 111.9, 52.2, 29.5, 21.7. HR-MS (ESI) [M+H]⁺ *m/z* calcd for C₂₆H₂₁ClN₄O 441.1477, found 441.1478.

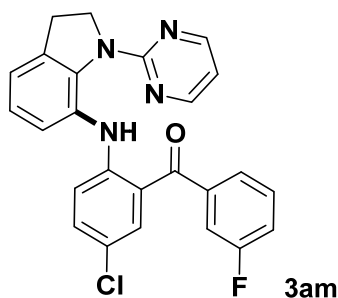


(5-chloro-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (4-fluorophenyl) methanone (3ak) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 76 mg (86%). Yellow solid. M.P. 175-177°C. ¹H NMR (CDCl₃, 400 MHz) δ 9.73 (s, 1H), 8.57 (m, 2H), 7.75 (m, 2H), 7.28 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.14 (m, 3H), 7.01 (m, 3H), 6.70 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 194.7, 165.3 (d, *J* = 253.6 Hz), 160.4, 158.5, 146.0, 137.3, 136.9, 135.3, 135.3, 133.2, 132.4 (d, *J* = 8.9 Hz), 132.2, 131.3, 124.7, 123.3 (d, *J* = 7.7 Hz), 121.2, 120.5,

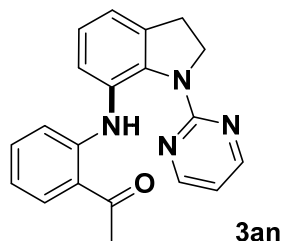
118.3, 115.6 (d, $J = 21.9$ Hz), 112.0, 52.3, 29.6. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{25}H_{18}ClFN_4O$ 445.1226, found 445.1126.



(5-chloro-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (3-methoxyphenyl) methanone (3al) : Eluent: petroleum ether/ ethyl acetate (10:1). Yield 72 mg (79%). Yellow solid. M.P. 164-166°C. 1H NMR ($CDCl_3$, 400 MHz) δ 9.84 (s, 1H), 8.58 (m, 2H), 7.36 (m, 1H), 7.33 (m, 1H), 7.23 (m, 3H), 7.14 (m, 1H), 7.09 (m, 1H), 7.01 (m, 3H), 6.70 (t, $J = 4.8$ Hz, 1H), 4.46 (t, $J = 7.9$ Hz, 2H), 3.86 (s, 3H), 3.11 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.0, 160.3, 159.6, 158.4, 146.1, 140.5, 137.3, 136.8, 133.1, 132.5, 131.1, 129.3, 124.5, 123.4, 123.0, 122.3, 120.8, 120.4, 118.0, 118.0, 114.3, 111.9, 55.6, 52.2, 29.5. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{26}H_{21}ClN_4O_2$ 457.1431, found 457.1432.

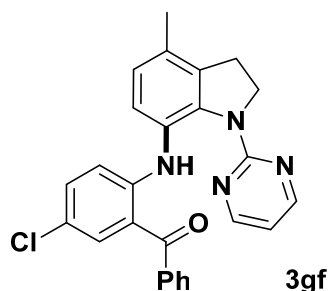


(5-chloro-2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (3-fluorophenyl) methanone (3am) : Eluent: petroleum ether/ ethyl acetate (10:1). Yield 62 mg (70%). Yellow solid. M.P. 175-177°C. 1H NMR ($CDCl_3$, 400 MHz) δ 9.91 (s, 1H), 8.59 (m, 2H), 7.43 (m, 3H), 7.30 (m, 1H), 7.24 (m, 2H), 7.16 (m, 1H), 7.02 (m, 3H), 6.73 (t, $J = 4.8$ Hz, 1H), 4.46 (t, $J = 7.9$ Hz, 2H), 3.12 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.7, 162.6 (d, $J = 248.0$ Hz), 160.3, 158.4, 146.4, 141.3 (d, $J = 6.3$ Hz), 137.4, 136.9, 133.5, 132.4, 130.9, 130.0 (d, $J = 7.6$ Hz), 125.4 (d, $J = 2.3$ Hz), 124.6, 123.5, 122.3, 120.9, 120.6, 118.9 (d, $J = 21.3$ Hz), 118.0, 116.3 (d, $J = 22.5$ Hz), 112.0, 52.2, 29.5. HR-MS (ESI) $[M+H]^+$ m/z calcd for $C_{25}H_{18}ClFN_4O$ 445.1226, found 445.1226.

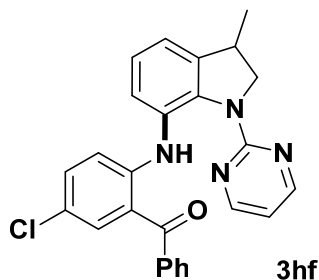


1-(2-((1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) ethan-1-one (3an) : Eluent: petroleum ether/ ethyl acetate (20:1). Yield 39 mg (60%). Yellow solid. M.P. 205-207°C. 1H NMR ($CDCl_3$, 400 MHz) δ 10.33 (s, 1H), 8.57 (m, 2H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.17 (m, 2H), 7.04 (m, 2H), 6.91 (d, $J = 8.5$ Hz, 1H), 6.71 (m, 1H), 6.61 (t, $J = 7.5$ Hz, 1H), 4.43 (t, $J = 8.6$ Hz, 2H), 3.11 (t, $J = 7.7$ Hz, 2H), 2.54

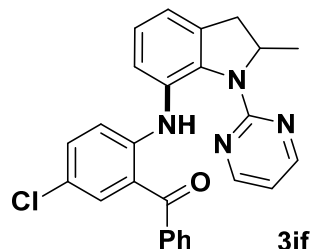
(d, $J = 1.9$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 199.6, 160.6, 158.3, 147.8, 138.2, 136.7, 133.8, 132.1, 131.0, 125.0, 124.4, 120.7, 120.6, 116.1, 115.6, 112.1, 52.3, 29.7, 28.3. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}$ 331.1553, found 331.1552.



(5-chloro-2-((4-methyl-1-(pyrimidin-2-yl)indolin-7-yl)amino)phenyl)(phenyl)methanone (3gf) :
 Eluent: petroleum ether/ ethyl acetate (20:1). Yield 77 mg (88%). Yellow solid. M.P. 116-118°C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.83 (s, 1H), 8.56 (m, 2H), 7.67 (m, 2H), 7.54 (m, 1H), 7.46 (m, 2H), 7.30 (m, 1H), 7.13 (m, 2H), 6.93 (d, $J = 9.1$ Hz, 1H), 6.88 (d, $J = 8.1$ Hz, 1H), 6.68 (t, $J = 4.8$ Hz, 1H), 4.45 (t, $J = 8.0$ Hz, 2H), 3.03 (t, $J = 7.9$ Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 196.4, 160.4, 158.4, 146.8, 139.4, 137.3, 135.1, 133.2, 132.7, 131.8, 130.1, 129.6, 128.4, 128.4, 125.7, 124.2, 122.2, 120.2, 117.5, 112.0, 52.0, 28.3, 18.6. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{26}\text{H}_{21}\text{N}_4\text{O}$ 441.1409, found 441.1412.

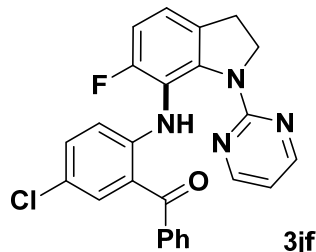


(5-chloro-2-((3-methyl-1-(pyrimidin-2-yl)indolin-7-yl)amino)phenyl)(phenyl)methanone (3hf) :
 Eluent: petroleum ether/ ethyl acetate (20:1). Yield 80 mg (91%). Yellow solid. M.P. 152-154°C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.83 (s, 1H), 8.57 (m, 2H), 7.69 (m, 2H), 7.55 (m, 1H), 7.46 (m, 2H), 7.31 (m, 1H), 7.25 (s, 1H), 7.14 (m, 1H), 7.04 (m, 2H), 6.96 (d, $J = 7.3$ Hz, 1H), 6.69 (t, $J = 4.8$ Hz, 1H), 4.67 (m, 1H), 3.91 (m, 1H), 3.42 (h, $J = 7.2$ Hz, 1H), 1.32 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 196.2, 160.5, 158.5, 146.1, 142.0, 139.1, 136.9, 133.1, 132.5, 132.0, 131.2, 129.7, 128.4, 124.7, 123.3, 123.3, 121.0, 119.0, 118.1, 111.9, 60.0, 36.0, 18.8. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{26}\text{H}_{21}\text{N}_4\text{O}$ 441.1477, found 441.1480.

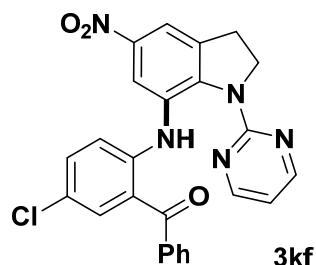


(5-chloro-2-((2-methyl-1-(pyrimidin-2-yl)indolin-7-yl)amino)phenyl)(phenyl)methanone (3if) :
 Eluent: petroleum ether/ethyl acetate (5:1). Yield 84 mg (95%). Yellow solid. M.P. 222-224°C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.83 (s, 1H), 8.56 (m, 2H), 7.69 (m, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.47 (m,

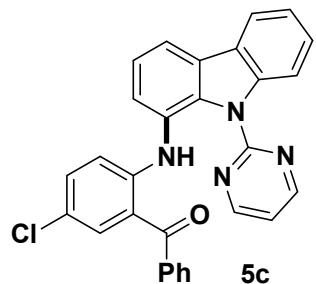
2H), 7.31 (m, 1H), 7.24 (m, 1H), 7.13 (m, 1H), 7.04 (m, 2H), 6.94 (d, $J = 9.1$ Hz, 1H), 6.69 (t, $J = 4.8$ Hz, 1H), 5.08 (p, $J = 6.7$ Hz, 1H), 3.48 (m, 1H), 2.57 (d, $J = 15.5$ Hz, 1H), 1.39 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 196.3, 159.9, 158.5, 146.4, 139.2, 136.1, 135.6, 133.1, 132.5, 131.9, 131.4, 129.7, 128.4, 124.6, 123.8, 122.9, 121.1, 120.7, 117.9, 112.1, 59.5, 36.7, 21.1. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{26}\text{H}_{21}\text{ClN}_4\text{O}$ 441.1409, found 441.1405.



(5-chloro-2-((6-fluoro-1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (phenyl) methanone (3jf) :
 Eluent: petroleum ether/ ethyl acetate (10:1). Yield 51mg (57%). Yellow solid. M.P. 153-155°C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.73 (s, 1H), 8.57 (m, 2H), 7.67 (m, 2H), 7.54 (m, 1H), 7.46(m, 2H), 7.31 (m, 1H), 7.17 (m, 1H), 7.00 (m, 1H), 6.85 (m, 1H), 6.74 (t, $J = 4.8$ Hz, 1H), 6.55 (m, 1H), 4.48 (t, $J = 8.0$ Hz, 2H), 3.09 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 196.7, 160.2, 157.4 (d, $J = 246.2$ Hz), 145.8, 140.2 (d, $J = 5.5$ Hz), 139.3, 133.3, 132.5, 131.9, 131.4, 131.4, 129.7, 128.4, 121.6, 120.8 (d, $J = 3.6$ Hz), 120.7, 119.1 (d, $J = 15.4$ Hz), 116.7 (d, $J = 2.7$ Hz), 112.5, 111.3 (d, $J = 21.6$ Hz), 53.1, 28.9. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{25}\text{H}_{18}\text{ClFN}_4\text{O}$ 445.1226, found 445.1228.



(5-chloro-2-((5-nitro-1-(pyrimidin-2-yl) indolin-7-yl) amino) phenyl) (phenyl) methanone (3kf) :
 Eluent: petroleum ether/ ethyl acetate (20:1). Yield 44 mg (47%). Yellow solid. M.P. 230-232°C. ^1H NMR (CDCl_3 , 400 MHz) δ 9.78 (s, 1H), 8.69 (m, 2H), 8.16 (m, 1H), 7.79 (m, 3H), 7.60 (m, 1H), 7.50 (m, 2H), 7.38 (m, 1H), 7.24 (m, 1H), 7.06 (d, $J = 8.9$ Hz, 1H), 6.87 (t, $J = 4.8$ Hz, 1H), 4.54 (t, $J = 8.2$ Hz, 2H), 3.21 (t, $J = 8.2$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 196.1, 159.7, 158.7, 149.2, 144.4, 142.3, 138.5, 137.6, 133.3, 132.6, 132.4, 131.4, 130.0, 128.6, 125.4, 123.1, 119.0, 118.6, 114.8, 113.3, 52.9, 28.7. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{25}\text{H}_{18}\text{ClN}_5\text{O}_3$ 472.1176, found 472.1180.



(5-chloro-2-((9-(pyrimidin-2-yl) -9H-carbazol-1-yl) amino) phenyl) (phenyl) methanone (5c) :
 Eluent: petroleum ether/ ethyl acetate (20:1). Yield 30 mg (32%). Yellow solid. M.P. 185-187°C. ^1H NMR (CDCl_3 , 400 MHz) δ 8.80 (m, 2H), 8.28 (d, $J = 8.3$ Hz, 1H), 8.09 (d, $J = 7.5$ Hz, 1H), 7.99 (d, $J =$

8.5 Hz, 1H), 7.63 (m, 2H), 7.57 (d, $J = 7.3$ Hz, 1H), 7.50 (m, 2H), 7.45 (m, 2H), 7.39 (m, 2H), 7.31 (d, $J = 2.5$ Hz, 1H), 7.07 (m, 2H), 6.67 (d, $J = 9.1$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 197.0, 158.5, 157.9, 147.2, 141.0, 139.1, 134.1, 133.9, 132.8, 131.7, 129.3, 128.5, 128.3, 127.5, 127.0, 125.4, 124.9, 122.9, 122.4, 120.4, 120.1, 119.9, 117.3, 117.0, 116.9, 113.3. HR-MS (ESI) $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{29}\text{H}_{19}\text{ClN}_4\text{O}$ 474.1247, found 474.1251.

The ^1H and ^{13}C NMR spectra of compounds 3.

