Supporting Information
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Supporting Information

Content
General remark
Experimental procedures
References
Analytical data for compounds
H NMR and C NMR spectra

General:
All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. 1H NMR and 13C NMR (300 or 400 MHz and 75 or 100MHz, respectively) spectra were recorded in CDCl3. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI.

General procedure for the preparation of 2-Chloro-1-methyl-1H-indole-3-carbaldehyde (A)[1]

POCl₃ (5.51mL) was added to a mixture of DMF (5.7mL) and CHCl₃ (20mL). A solution of 1-methylindolin-2-one (18mmol) in CHCl₃ (20mL) was then added. The
mixture was boiled for 18 h, cooled and poured onto water. Then the PH of the mixture was adjusted to PH=7 with sodium carbonate. The whole was extracted with dichloromethane. The organic layer was washed with brine, dried over Na2SO4, and evaporated under reduced pressure. The products were separated by column chromatography (silica gel, hexane–acetone, 10:1) to afford the title compound (78%) . The identity and purity of the product was confirmed by 1H and 13C NMR spectroscopic analysis.

General procedure for the preparation of (E)-4-(2chloro-1-methyl-1H-indol-3-yl)but-3-en-2-one (B) from (A) [2]

![Chemical structure](image)

The (9a) (43.2 mmol) was added gradually to a solution of NaOH (2.2 g) in H2O (20.0 ml) and ketone (43.3 mmol) in ethanol (12 ml) at 0 °C. The reaction mass was stirred at room temperature for 4 h. After 4 h, satd NH4Cl solution was added to the flask, followed by extraction with ether. The combined organic layers were dried over Na2SO4 and concentrated to give a solid which was washed successively with hexane to give pure (9b). (9b) was obtained as a yellow solid after being purified.

General procedure for the preparation of (1b) from (B). [3]

![Chemical structure](image)

A mixture of (9b) (0.01 mol), acetic acid (20 ml) and phenylhydrazine (0.01 mol) was refluxed for 12 h. The resulting mixture was cooled to 283 K and filtered. The progress of the reaction and the purity of the products were monitored by thinlayer chromatography. The crude products thus obtained were recrystallized from propan-2-ol.

Photochemical Reactions; General Procedure:

1a (0.070 g, 0.3 mmol) was dissolved in 25 mL dry acetone. The solution was deaerated by bubbling Ar for 30 min and irradiated at \( \lambda \geq 300 \) nm with a high-pressure mercury lamp (500 W) at ambient temperature. The progress of reaction was monitored by TLC at regular intervals. After the solvent was removed under reduced
pressure, the residue was separated by column chromatography on silica gel eluted by hexane–ethyl acetate 10 : 1 ( v/v ) to afford products 4a. The solid was further purified by recrystallization from ethyl acetate.

Reference:


Analytical data for compounds

1-methyl-3-(3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)-1H-indol (1a)

White oil

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 2.083(s, 3H, CH$_3$) 2.844(q, J=1.7HZ, 1H) 3.441(q, J=1.7HZ, 1H) 3.689(s, 3H, NCH$_3$) 5.285(q, J=1.7HZ, 1H) 6.727(q, J=7.5HZ, 1H) 6.917(s, 1H) 7.046(d, J=7.5HZ, 2H) 7.059-7.163(m, 3H) 7.231(d, J=5.1HZ, 1H) 7.303(d, J=8.1HZ, 1H) 7.587(d, J=7.2HZ, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 16.11(CH$_3$) 32.76(NCH$_3$) 46.58(CH$_2$) 57.92(CH) 109.52(CH) 113.26(CH) 115.87(CH) 118.40(CH) 119.03(CH) 119.15(CH) 121.85(CH) 125.55(C) 126.29(CH) 128.76(CH) 137.51(C) 146.57(C) 149.52(C) 207.04(C)

1-methyl-3-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-1H-indol (1a-b)

White oil

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 2.417(s,3H, CH$_3$) 3.685(s, 3H CH$_3$) 6.409(s, 1H) 6.687(s, 1H) 7.112(t, J=4.5HZ, 1H) 7.216-7.372(m, 5H) 7.400(d, J=1.8HZ, 2H) 7.540(d, J=8.4HZ, 1H)

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 13.642(CH$_3$) 31.686(CH$_3$) 32.865(CH) 53.671(CH) 105.144(CH) 107.056(CH) 109.337(CH) 119.983(CH) 120.063(CH) 122.116(CH) 125.077(CH) 126.355(CH) 126.950(CH) 128.057(CH) 128.694(CH) 136.531(CH) 137.657(CH) 140.557(CH) 149.432(CH)
2-chloro-1-methyl-3-(3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)-1H-indole (1b)

Yellow solid, mp=129-130°C
$^1$H NMR (400 MHz, CDCl3): $\delta$ =2.155(s, 3H, CH$_3$) 2.901(d, J=1.8, 1H) 3.354(m, J=1.8Hz, 1H) 3.724(s,3H, NCH$_3$) 5.343(d, J=1.3Hz 1H) 6.676(t, J=7.2Hz 1H) 6.997-7.119(m,5H) 7.180(t, J=7.6Hz, 1H) 7.273(d, J=1.5Hz, 1H) 7.508(d, J=8Hz, HZ)
$^{13}$C NMR (100 MHz, CDCl3): $\delta$=15.99(CH$_3$) 29.84(NCH$_3$) 45.23(CH$_2$) 57.00(CH) 109.29(CH) 111.10(C) 113.00(CH) 118.50(CH) 119.18(C) 120.24(CH) 122.20(CH) 123.15(C) 124.28(C) 128.81(CH) 36.15(C) 146.36(C) 148.78(C)

2-chloro-1-methyl-3-(methyl-1-phenyl-1H-pyrazol-5-yl)-1H-indole (1b-a)

White solid, mp=168-169°C
$^1$H NMR (400 MHz, CDCl3): $\delta$ =2.442(s, 3H, CH$_3$) 3.703(s, 3H, CH$_3$) 6.379(s, 1H) 7.179-7.327(m, 8H)
$^{13}$C NMR (100 MHz, CDCl3): $\delta$=30.27(CH$_3$) 30.23(CH$_3$) 103.18(C) 109.43(CH) 109.56(CH) 109.60(CH) 119.33(CH) 121.01(CH) 122.65(CH) 123.80(CH) 125.57(C) 126.23(C) 126.69(C) 128.88(CH) 135.27(C) 135.79(C) 140.87(CH) 149.74(C)
$^1$H NMR and $^{13}$C NMR spectra:

2a
2d
4c