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Rhodium(III)-catalyzed C-H alkylation of heterocycles with allylic alcohols in water: A reusable catalytic system for the synthesis of β-aryl ketones

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ABSTRACT

A highly efficient, green and sustainable protocol for rhodium(III)-catalyzed C-H alkylation of heterocycles with allylic alcohols has been achieved, which affords a series of β-aryl ketones in high yields. The reaction proceeds smoothly in water under air, and works well with heterocycles such as indoles, indolines, pyrroles and carbazoles. Notably, the expensive rhodium catalyst in water could be easily separated from the organic products, and reused for at least five times without loss of its catalytic activity and selectivity, which is a promising, green and sustainable pathway for the synthesis of β-aryl ketones. To the best of our knowledge, this is the first example for the reuse of expensive rhodium catalyst in water.

1. Introduction

The β-aryl ketones are important building blocks in organic synthesis, medicinal chemistry and natural products [1]. During the last few decades, considerable research efforts have been devoted to develop efficient methods for the preparation β-aryl ketones, and many strategies have been established. However, methods such as conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds [2], or Heck-type couplings of aryl nucleophiles with allylic alcohols, usually required pre-functionalized arylboronic acids, arylhalides or aryldiazonium salts as arenes sources [3], which suffered from poor atom-economy and limited substrate scope. Therefore, step- and atom-economic synthetic methods for the synthesis of β-aryl ketones is highly desired.

Transition-metal-catalyzed C-H functionalization has emerged as a powerful tool for the construction of C-C bonds [4]. Preparation of β-aryl ketones using rhodium(III)-catalyzed C-H bond alkylation has attracted increasing attention due to its high efficiency and selectivity [5]. For example, rhodium(III)-catalyzed conjugate addition of aryl C-H bond to α,β-unsaturated carbonyl compounds represents one of the most powerful tools for the preparation of β-aryl ketones, and many efficient methods have been well established by Li, Huang, Loh, Ellmann, Glorius, Ackermann and other's group [6]. Transition-metal-catalyzed C-H alkylation with allylic alcohols is another efficient route to prepare β-aryl ketones [7]. In 2013, Jiang and coworkers successfully fulfilled the rhodium(III)-catalyzed oxidative alkylation of aryl C-H bonds using the electronically nonbiased allylic alcohols to prepare the functionalized β-aryl ketones [8]. Meanwhile, Glorius and coworkers also reported the oxidative alkylation of indoles with the allylic alcohols to generate β-indolyl aldehydes [9]. Kim and coworkers reported the alkylation of indolines with allylic alcohols [10]. Despite of considerable advances in this field, the reported methods still suffered from three major limitations: 1) the reaction usually required excess copper salts; 2) the reaction performed in toxic organic solvents; 3) the catalytic system could not be reused. Therefore, to explore more efficient, green and environmental benign process is still of great importance.

In order to overcome these limitations, synthesis of organic compounds using environmental friendly solvents or recyclable catalytic systems have gained great interests in recent years [11].

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0040-4020/

The recyclable catalytic system using metals in PEGs has been well studied, while catalysis in water is rarely involved [12]. Given water is the most inexpensive, non-flammable and environmentally benign solvent, and the water phase containing cationic metal catalyst is easily separated from organic compounds, development of organic reactions in water is becoming an area of crucial importance in modern chemistry. Although there has been considerable efforts dedicated to the development of organic reactions in water [13], Rh(III)-catalyzed C-H functionalization using water as solvent is rarely explored. Recently, the groups of Zhu, Li, Hong reported Rh(III)-catalyzed C-H alkylation or annulation reactions in water [14], however, the recyclability and reusability of noble rhodium catalyst were not involved. Considering the high cost of the rhodium catalyst, it is highly desirable to develop cost-effective and recyclable rhodium catalytic system. With our continuing interest in the green and sustainable chemistry using water as the solvent [15], herein, we report the first reusable rhodium(III)/H_2O catalytic system for C-H alkylation of heterocycles with allylic alcohols, which proceeds smoothly under mild conditions, and affords the desired β-aryl ketones in high yields (Scheme 1).

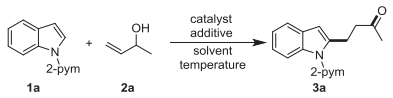
2. Results and discussion

We commenced our investigation by selecting (pyrimidin-2-yl)-1H-indole (**1a**) and but-3-en-2-ol (**2a**) as model substrates to evaluate the reaction conditions (Table 1). Using 2.5 mol% of $[Cp^*RhCl_2]_2$ as the catalyst in water at room temperature, the reaction gave the desired product **3a** in 10% yield (Table 1, entry 1). The additives played an important role in this reaction, among a number of additives examined, silver salt $AgSbF_6$ was proved to be the best and the desired product was obtained in 65% yield (Table 1, entries 2–6). When the reaction was performed at 80 °C, the yield was significantly improved, and the product **3a** was obtained in 92% yield (Table 1, entries 7–9). Finally, some control experiments were performed, surprisingly, the reaction could take place in neat conditions, and product was obtained in a moderate yield of 40% (Table 1, entry 10). When the catalyst loading was reduced to 1 mol %, the yields was sharply decreased, increasing the amount of catalyst to 5 mol% did not improve the yield (Table 1, entries 11 and 12). Switching the catalyst to other common used metal catalysts such as $[Ru(cy\text{-}mene)Cl_2]_2$, $[Cp^*IrCl_2]_2$, $Cp^*Co(CO)I_2$ or $Pd(OAc)_2$, the reaction did not occur at all (Table 1, entries 13–16). In addition, when the reaction was performed under O_2 atmosphere, 91% yield was obtained, while a N_2 atmosphere suppressed the reaction, which suggested that oxygen in air may be the oxidant of this process (Table 1, entries 17 and 18).

With the optimized conditions in hand, the substrate scope of indoles were first explored and the results were summarized in Scheme 2. Both electron-withdrawing (e.g., Cl, Br, F, COOMe) and electron-donating groups (e.g., CH_3, OCH_3, OBn) on the indoles were all well tolerated, affording the corresponding product in high yields (**3a**-**3j**). Especially, the indoles bearing halogen atoms at C4, C5 or C6 position provided potential opportunities for further transformations of these products (**3b**-**3e**). It was noteworthy that the steric hindered indole bearing a methyl group on C3 position was also successfully converted to desired product in a high 82% yield (**3j**). C7-substituted indole was also checked, and the product was obtained in 65% yield (**3k**). When the directing group was switched from N-pyrimidyl to N-pyridyl, a sharply decreased yield of 55% was obtained (**3l**). In addition, the substrate scope was not limited to the indoles, N-pyrimidyl indoline and N-pyrimidyl carbazole reacted well with but-3-en-2-ol (**2a**), leading to the C7 and C3-selective alkylated products in 80% and 72% yield, respectively (**3n** and **3o**). It is notable that when (pyrimidin-2-yl)-1H-pyrrole was used as substrate, the mono-alkylated product **3m** was isolated in 75% yield. These results further revealed the broad application and high site-selectivity of this chemistry. Unfortunately, other directing groups such as Ac, Piv or Ts failed to give the desired products, probably due to their weak coordination effect (**3p**-**3r**).

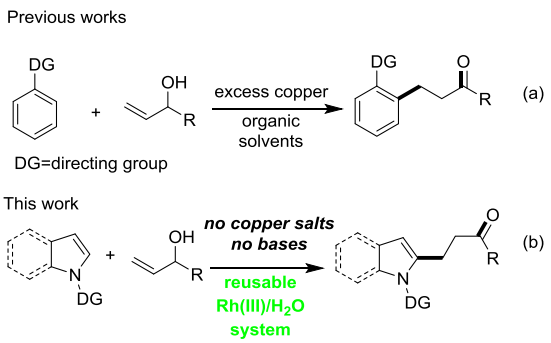
The scope with respect to allylic alcohols was next explored. As shown in Scheme 3, various α-substituted allylic alcohols were tolerated in this reaction. Linear allylic alcohols were successfully converted into the desired β–aryl ketones in high yield (**4a**, **4b**, **4f** and **4g**), while the branched allylic alcohol **2c** only gave a 45% yield of desired product (**4c**). Allylic alcohols bearing an aliphatic ring were also tolerated in the reaction, and the desired products were obtained in 82% and 84% yield, respectively (**4d** and **4e**). Importantly, α-aryl substituted allylic alcohols were all smoothly converted into the desired product in high yields (**4h**-**4k**). Unfortunately, when allylic alcohols with pyridyl was used as the

Table 1
Optimization of the reaction Conditions[a,b].



entry	catalyst	additive	t (°C)	yield (%)[b]
1	$[Cp^*RhCl_2]_2$	–	RT	10
2	$[Cp^*RhCl_2]_2$	NaOAc	RT	19
3	$[Cp^*RhCl_2]_2$	AgOAc	RT	25
4	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	RT	45
5	$[Cp^*RhCl_2]_2$	AgOTf	RT	50
6	$[Cp^*RhCl_2]_2$	$AgSbF_6$	RT	65
7	$[Cp^*RhCl_2]_2$	$AgSbF_6$	60	88
8	$[Cp^*RhCl_2]_2$	$AgSbF_6$	80	92
9	$[Cp^*RhCl_2]_2$	$AgSbF_6$	100	90
10[c]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	80	40
11[d]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	80	55
12[e]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	80	90
13	$[Ru(cy\text{-}mene)Cl_2]_2$	$AgSbF_6$	80	0
14	$[Cp^*IrCl_2]_2$	$AgSbF_6$	80	0
15	$Cp^*Co(CO)I_2$	$AgSbF_6$	80	0
16	$Pd(OAc)_2$	$AgSbF_6$	80	0
17[f]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	80	91
18[g]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	80	trace

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (2.5 mol%), additive (10 mol%) in H_2O (2 mL) under air for 12 h.
[b] Isolated yield.
[c] Without solvent.
[d] 1 mol% of catalyst was used.
[e] 5 mol% of catalyst was used.
[f] Under O_2 atmosphere.
[g] Under N_2 atmosphere.



Scheme 1. C-H alkylation of arenes with allylic alcohols.

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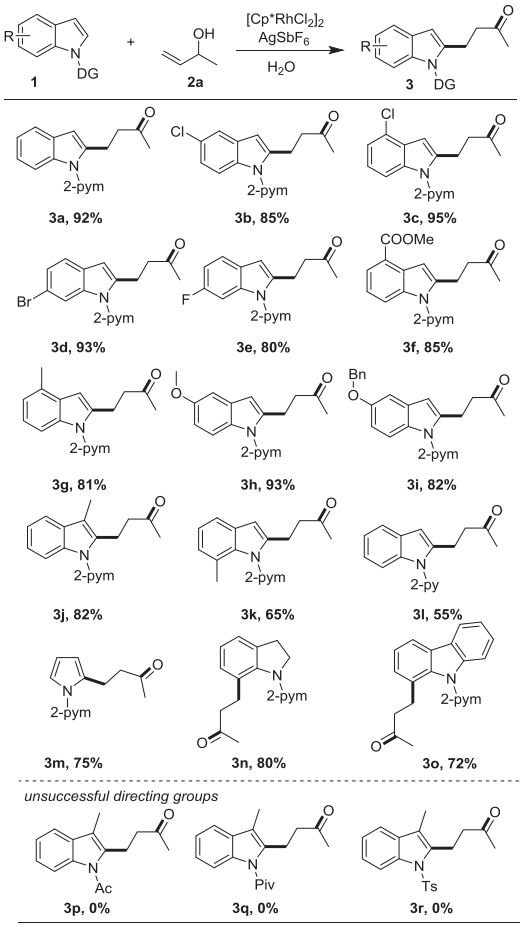

[a] Reaction Conditions: 1 (0.20 mmol), 2a (0.40 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) in H_2O (2 mL) at 80 °C for 12 h. [b] Isolated yield.

Scheme 2. Scope of indoles[a,b].
[a] Reaction Conditions: 1 (0.20 mmol), 2a (0.40 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) in H_2O (2 mL) at 80 °C for 12 h. [b] Isolated yield.

partner, the reaction did not occur (**4l**).

To highlight the synthetic value of this process, the scale-up experiment was also performed, and the desired product was obtained in 83% yields (Scheme 4).

The aim of this process is to develop a green and sustainable method for the synthesis of β-aryl ketones using water as the solvent, therefore, we next turn our attention to test the reusability of this catalytic system using the reaction of (pyrimidin-2-yl)-1H-indole (**1a**) and but-3-en-2-ol (**2a**) under standard conditions. After the first cycle, the reaction mixture was extracted with ethyl acetate (3*10 mL), the aqueous phase was separated as a clear yellow liquid (Fig. 1). Then the separated aqueous phase was recharged with fresh (pyrimidin-2-yl)-1H-indole (**1a**) and but-3-en-2-ol (**2a**) for the next run, and the results were shown in Fig. 2. Pleasingly, we found that the catalytic system could be reused for at least five times without obvious loss of the catalytic activity. However, after the fifth cycle, the color of aqueous phase became shallow, and as expected, in the sixth cycle, the yield decreased sharply to a moderate 55% yield. It is worth mentioning that the separated rhodium/H_2O system is still of high catalytic efficiency without recharging the silver salt. Additionally, the catalytic system could be prepared under standard conditions using 2.5 mol% of $[Cp^*RhCl_2]_2$ and 10 mol% $AgSbF_6$. The result solution was charged with substrates **1a** and **2a**, and the product **3a** was obtained in 83% yield. These results suggested that the active rhodium species formed in the reaction should be homogenerous and soluble in water, which could be easily separated from the organic phase and reused directly for the next run.

Although the mechanism of this process is not clear, some control experiments were performed to gain insights into the mechanism of this reaction (Scheme 5). The H/D exchange experiment was first examined with D_2O as the solvent and an obvious H/D exchange at C2 position was observed, indicating that the C-H bond cleavage is reversible. The intermolecular competition experiments between electron-rich and electron-deficient indoles revealed that the indoles bearing electron-donating groups is more reactive. The reaction with two different allylic alcohols was also performed, and we found allylic alcohols bearing an aromatic ring were less reactive.

On the basis of our experiments and previous reports [16], a plausible catalytic cycle was outlined in Scheme 6. First, the cationic Rh(III) catalyst formed from $[Cp^*RhCl_2]_2$ and $AgSbF_6$, followed by coordination with **1a** to generate a five-member rhodacycle **I**. Then insertion of the allyl alcohol **2a** to rhodacycle **I** generated the

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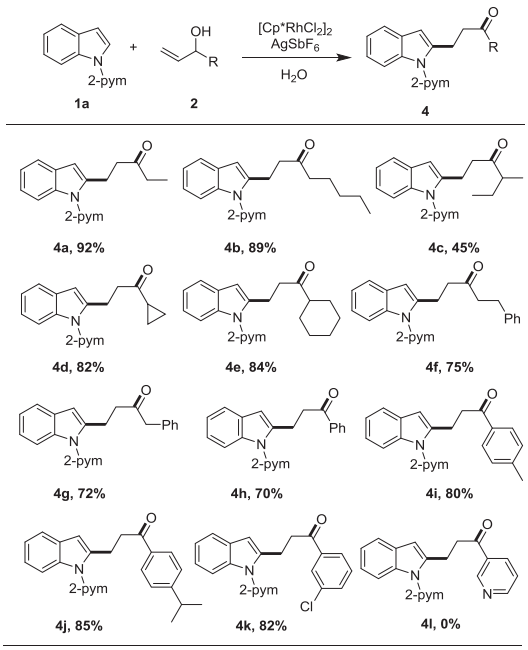
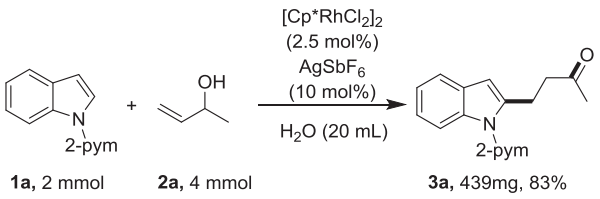


[a] Reaction Conditions: 1a (0.20 mmol), 2 (0.40 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) in H_2O (2 mL) at 80 °C for 12 h. [b] Isolated yield.

Scheme 3. Scope of allylic alcohols [a,b].

[a] Reaction Conditions: 1a (0.20 mmol), 2 (0.40 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) in H_2O (2 mL) at 80 °C for 12 h. [b] Isolated yield.



Scheme 4. Scale-up experiment.

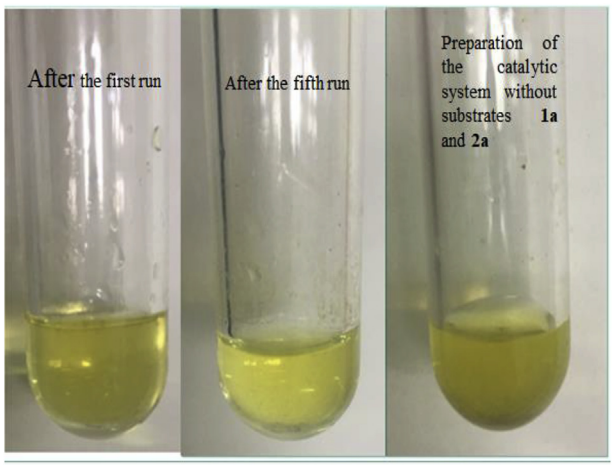


Fig. 1. The color of separated catalytic system.

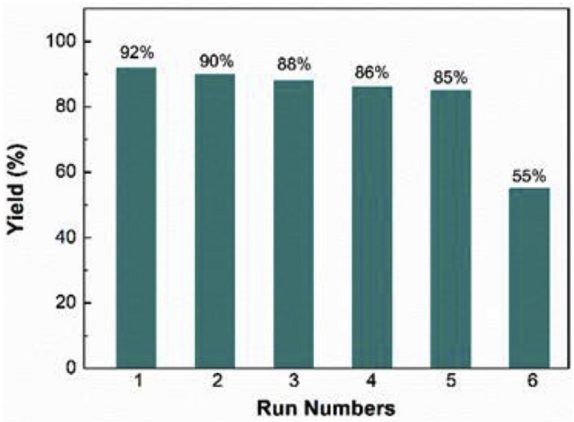


Fig. 2. Reusability experiments of catalytic system.

intermediated **II**, which underwent β-H elimination to afford the corresponding enol product **C**. Subsequently keto−enol tautomerization of **C** gave β-aryl ketone **3a**. The Rh(III)-H species obtained from β-H elimination of **II** underwent the reductive elimination and reoxidation to regenerate the active Rh(III) catalyst to finish the catalytic cycle[16e,f,g].

3. Conclusions

In conclusion, we have developed an efficient, green and sustainable protocol for Rh(III)-catalyzed C-H alkylation of various heterocycles with allylic alcohols, various β-aryl ketones were prepared in high yields. The reaction proceeded smoothly in water, and exhibited high regioselectivity, and good functional group

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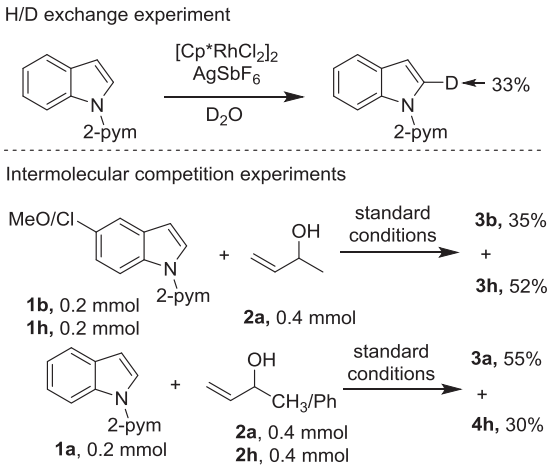
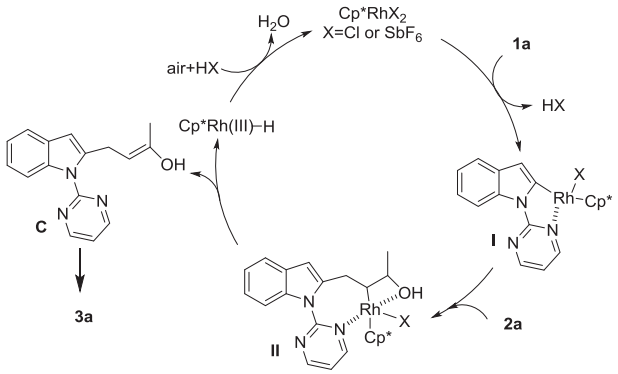


Scheme 5. Control experiments.



Scheme 6. Proposed reaction mechanism.

tolerance. Notably, this Rh(III)/H_2O catalytic system could be reused for at least five times without loss of catalytic activity, thus providing an efficient, environmental friendly process for the synthesis of β-aryl ketones.

4. Experimental

Unless otherwise noted, all reactions were performed in air, all reagents and solvents were obtained from commercial suppliers and used without any purification. Purifications of reaction products were carried out by chromatography using silica gel (200–300 mesh). NMR spectra were recorded for ^{1}H NMR at 400 MHz and for ^{13}C NMR at 100 MHz. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard (δ = 0) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR, TMS (δ = 0) or $CDCl_3$ (δ = 77.26) was used as internal standard and spectra were obtained with complete proton decoupling.

Substituted indoles [17], pyrrol [17], indoline [18], carbazoles [19] and allylic alcohols [20] were prepared according to the literature.

4.1. General procedure for the alkylation of heterocycles

Heterocycles **1** (0.2 mmol, 1.0 equiv), allylic alcohols **2** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (0.02 mmol, 10 mol %) and H_2O (2 mL) were charged into a Schlenk tube under air. The reaction mixture was stirred for 12 h at 80 °C. After the reaction was complete, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was purified by flash chromatography on silica gel using hexane/ethyl acetate as the eluent to give the pure product **3**.

4.2. 4-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (*3a*) [9]

Yield: 92%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.53–7.51 (m, 1H), 7.25–7.12 (m, 3H), 6.45 (s, 1H), 3.42 (t, *J* = 7.8 Hz, 2H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.0, 158.2, 140.5, 136.9, 129.2, 122.8, 122.0, 119.8, 117.1, 114.1, 106.0, 43.5, 30.0, 23.8. **HRMS (ESI+)** calcd for $C_{16}H_{16}N_3O$ **[M+H]$^+$**: 266.1288, found: 266.1286.

4.3. 4-(5-Chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (*3b*)

Yield: 85%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 4.8 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.10–7.08 (m, 2H), 6.30 (s, 1H), 3.34 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.7, 157.2, 141.0, 134.2, 129.3, 126.3, 121.7, 118.1, 116.3, 114.3, 104.3, 42.2, 28.8, 22.7, 13.1. **HRMS (ESI+)** calcd for $C_{16}H_{15}ClN_3O$ **[M+H]$^+$**: 300.0898, found: 300.0899.

4.4. 4-(4-Chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (*3c*)

Yield: 95%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.12–7.06 (m, 3H), 6.49 (s, 1H), 3.34 (t, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 7.8 Hz, 2H), 2.12 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.6, 157.0, 140.4, 136.5, 126.8, 123.9, 122.3, 120.6, 116.6, 111.6, 102.8, 42.2, 28.8, 22.5. **HRMS (ESI+)** calcd for $C_{16}H_{15}ClN_3O$ **[M+H]$^+$**: 300.0898, found: 300.0901.

4.5. 4-(6-Bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (*3d*)

Yield: 93%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (d, *J* = 4.8 Hz, 2H), 8.50 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.30–7.26 (m, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 6.41 (s, 1H), 3.42–3.38 (m, 2H), 2.89 (t, *J* = 7.8 Hz, 2H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.8, 158.1, 141.3, 137.5, 128.0, 125.1, 120.8, 117.3, 116.4, 105.9, 43.3, 32.0, 30.1, 29.5, 23.2, 14.2. **HRMS (ESI+)** calcd for $C_{16}H_{15}BrN_3O$ **[M+H]$^+$**: 344.0393, found: 344.0395.

4.6. 4-(6-Fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (*3e*)

Yield: 80%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 4.8 Hz, 2H), 8.04–8.01 (m, 1H), 7.35–7.32 (m, 1H), 7.10 (t, *J* = 4.8 Hz, 1H), 6.90–6.85 (m, 1H), 6.34 (s, 1H), 3.35 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.9, 160.3, 158.0, 157.2, 140.0, 135.9, 124.5, 119.1, 116.2, 109.1, 104.8, 100.6, 42.4, 29.0, 22.9. **HRMS (ESI+)** calcd for $C_{16}H_{15}FN_3O$ **[M+H]$^+$**: 284.1194, found: 284.1194.

4.7. Methyl 2-(3-oxobutyl)-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate (*3f*)

Yield: 85%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.95–7.93 (m, 1H), 7.28-7.17 (m, 3H), 3.99 (s, 3H), 3.44 (t, *J* = 7.1 Hz, 3H), 2.98 (t, *J* = 7.9 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.7, 158.1, 143.0, 137.6, 129.2, 124.9,

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122.0, 120.5, 118.5, 117.7, 106.3, 51.8, 43.2, 30.0, 23.6. **HRMS (ESI+)** calcd for $C_{18}H_{18}N_3O_3$ **[M+H]**$^+$: 324.1343, found: 324.1345.

*4.8. 4-(4-Methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (**3g**)*

Yield: 81%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79 (d, J = 4.8 Hz, 2H), 8.14 (d, J = 8.4 Hz, 1H), 7.19-7.13 (m, 2H), 7.02 (d, J = 7.2 Hz, 2H), 6.51 (s, 1H), 3.45 (t, J = 7.2 Hz, 2H), 2.93 (t, J = 7.8 Hz, 2H), 2.56 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.4, 158.1, 136.1, 135.6, 130.4, 123.0, 121.7, 118.0, 116.7, 114.1, 113.5, 43.9, 29.7, 20.9, 8.8. **HRMS (ESI+)** calcd for $C_{17}H_{18}N_3O$ **[M+H]**$^+$: 280.1444, found: 280.1449.

*4.9. 4-(5-Methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (**3h**)*

Yield: 93%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (d, J = 4.8 Hz, 2H), 8.18 (d, J = 9.0 Hz, 1H), 7.04 (s, 1H), 6.91 (d, J = 2.6 Hz, 1H), 6.80−6.77 (m, 1H), 6.30 (s, 1H), 3.78 (s, 3H), 3.36 (t, J = 7.1 Hz, 2H), 2.82 (t, J = 7.8 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.0, 157.1, 154.4, 140.2, 130.7, 128.9, 115.7, 114.3, 110.6, 105.2, 101.1, 54.7, 42.5, 29.0, 23.0. **HRMS (ESI+)** calcd for $C_{17}H_{18}N_3O_2$ [**M+H**]$^+$: 296.1394, found: 296.1396.

*4.10. 4-(5-(Benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (**3i**)*

Yield: 82%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (d, J = 4.8 Hz, 2H), 8.26 (d, J = 9.1 Hz, 1H), 7.48−7.26 (m, 6H), 7.13−7.06 (m, 2H), 6.95−6.92 (m, 1H), 6.37 (s, 1H), 5.12 (s, 2H), 3.43 (t, J = 7.1 Hz, 2H), 2.89 (t, J = 7.8 Hz, 2H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.1, 158.1, 154.6, 141.3, 137.6, 131.9, 130.0, 128.6, 127.8, 127.5, 116.8, 115.3, 112.5, 106.2, 103.7, 70.6, 43.6, 30.0, 24.1. **HRMS (ESI+)** calcd for $C_{23}H_{22}N_3O_2$ [**M+H**]$^+$: 372.1707, found: 372.1719.

*4.11. 4-(3-Methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (**3j**)*

Yield: 82%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (d, J = 4.8 Hz, 2H), 8.35−8.32 (m, 1H), 7.54−7.51 (m, 1H), 7.28-7.24 (m, 2H), 7.14-7.10 (m, 1H), 3.40 (t, J = 7.8 Hz, 2H), 2.85 (t, J = 7.8 Hz, 2H), 2.32 (s, 3H), 2.16 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.5, 158.2, 136.0, 135.6, 130.4, 123.0, 121.7, 118.0, 116.7, 114.1, 113.5, 43.9, 30.0, 20.9, 8.8. **HRMS (ESI+)** calcd for $C_{17}H_{18}N_3O$ **[M+H]**$^+$: 280.1444, found: 280.1446.

*4.12. 4-(7-Methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (**3k**)*

Yield: 65%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (d, J = 4.8 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 4.8 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 2H), 2.97-2.93 (m, 2H), 2.91-2.87 (m, 2H), 2.17 (s, 3H), 1.95 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.0, 158.0, 140.2, 136.2, 129.0, 124.6, 121.2, 120.8, 118.8, 117.5, 102.7, 42.4, 29.5, 21.2, 19.4. **HRMS (ESI+)** calcd for $C_{17}H_{18}N_3O$ **[M+H]**$^+$: 280.1444, found: 280.1448.

*4.13. 4-(1-(Pyridin-2-yl)-1H-indol-2-yl)butan-2-one (**3l**)*

Yield: 55%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53-8.51 (m, 1H), 7.83-7.79 (m, 1H), 7.34-7.32 (m, 3H), 7.03−7.01 (m, 1H), 6.25 (t, J = 3.2 Hz, 1H), 6.08 (s, 1H), 3.12 (t, J = 7.2 Hz, 2H), 2.81 (t, J = 8.0 Hz,2H), 2.16 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.4, 152.8, 148.9, 138.5, 138.0, 132.7, 127.4, 121.2, 120.7, 117.3, 109.3, 109.1, 43.6, 30.0, 22.0. **HRMS (ESI+)** calcd for $C_{17}H_{17}N_2O$ **[M+H]**$^+$: 265.1335, found: 265.1337.

*4.14. 4-(1-(Pyrimidin-2-yl)-1H-pyrrol-2-yl)butan-2-one (**3m**)*

Yield: 75%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, J = 4.8 Hz, 2H), 7.77-7.75 (m, 1H), 7.10-7.07 (m, 1H), 6.22 (t, J = 3.2 Hz, 1H), 6.08 (s, 1H), 3.39 (t, J = 7.8 Hz, 2H), 2.86 (t, J = 8.0 Hz, 2H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.7, 158.1, 133.9, 120.9, 117.0, 111.7, 109.9, 43.9, 30.0, 24.0. **HRMS (ESI+)** calcd for $C_{12}H_{14}N_3O$ **[M+H]**$^+$: 216.1131, found: 216.1133.

*4.15. 4-(1-(Pyrimidin-2-yl)indolin-7-yl)butan-2-one (**3n**) [10]*

Yield: 80%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (d, J = 4.8 Hz, 2H), 7.04 (d, J = 6.9 Hz, 1H), 7.00-6.93 (m, 2H), 6.63 (t, J = 4.8 Hz, 1H), 4.35 (t, J = 7.6 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.84−2.80 (m, 2H), 2.68−2.64 (m, 2H), 1.98 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.7, 161.3, 157.7, 142.4, 135.2, 131.0, 128.2, 124.5, 122.5, 112.4, 53.4, 43.1, 29.9, 29.7, 28.2. **HRMS (ESI+)** calcd for $C_{16}H_{18}N_3O$ **[M+H]**$^+$: 268.1444, found: 268.1446.

*4.16. 4-(9-(Pyrimidin-2-yl)-4b,8a-dihydro-9H-carbazol-1-yl) butan-2-one (**3o**) [10]*

Yield: 72%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.81 (d, J = 4.8 Hz, 2H), 8.00−7.90 (m, 3H), 7.37−7.33 (m, 1H), 7.26−7.19 (m, 4H), 2.83 (t, J = 7.5 Hz, 2H), 2.58−2.54 (m, 2H), 1.91 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.9, 157.8, 157.6, 140.3, 137.0, 127.2, 125.9, 125.8, 125.6, 124.4, 121.2, 118.9, 117.3, 117.2, 111.2, 42.1, 28.9, 27.0. **HRMS (ESI+)** calcd for $C_{20}H_{18}N_3O$ **[M+H]**$^+$: 316.1444, found: 316.1446.

*4.17. 1-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)pentan-3-one (**4a**) [21]*

Yield: 92%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 8.3 Hz, 1H), 7.53−7.51 (m, 1H), 7.26−7.18 (m, 3H), 6.45 (s, 1H), 3.43 (t, J = 7.8 Hz, 2H), 2.87 (t, J = 7.8 Hz, 2H), 2.45 (q, J = 7.8 Hz, 2H), 1.07 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 210.7, 158.2, 140.7, 136.9, 129.2, 122.8, 121.9, 119.8, 117.1, 114.1, 106.0, 42.2, 36.0, 23.8, 7.9. **HRMS (ESI+)** calcd for $C_{17}H_{18}N_3O$ **[M+H]**$^+$: 280.1444, found: 280.1446.

*4.18. 1-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)octan-3-one (**4b**) [21]*

Yield: 89%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 7.6 Hz, 1H), 7.53−7.51 (m, 1H), 7.26−7.13 (m, 3H), 6.45 (s, 1H), 3.41 (t, J = 7.4 Hz, 2H), 2.86 (t, J = 7.6 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 1.58 (t, J = 7.5 Hz, 2H), 1.29−1.24 (m, 4H), 0.89 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 210.4, 158.2, 140.7, 136.9, 129.2, 122.8, 121.9, 119.8, 117.1, 114.1, 106.0, 42.7, 31.4, 29.7, 23.7, 22.5, 14.0. **HRMS (ESI+)** calcd for $C_{20}H_{24}N_3O$ **[M+H]**$^+$: 322.1914, found: 322.1916.

*4.19. 4-Methyl-1-(1-(pyrimidin-2-yl)-1H-indol-2-yl)hexan-3-one (**4c**)*

Yield: 55%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (d, J = 4.8 Hz, 2H), 8.31 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.27−7.16 (m, 3H), 6.48 (s, 1H), 3.42 (t, J = 7.8 Hz, 2H), 2.95−2.91 (m, 2H), 2.54−2.45 (m, 1H), 1.74-1.66 (m, 1H), 1.45-1.38 (m, 1H), 1.09 (d, J = 7.2 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.8, 158.2, 140.8, 136.9, 129.2, 122.7, 121.9, 119.7, 117.1, 114.0, 106.0, 47.9, 41.1, 26.0, 23.6, 15.9, 117.7. **HRMS (ESI+)** calcd for $C_{19}H_{22}N_3O$ **[M+H]**$^+$: 308.1757, found: 308.1759.

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*4.20. 1-Cyclopropyl-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)propan-1-one (**4d**) [22]*

Yield: 82%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 8.4 Hz, 1H), 7.54–7.52 (m, 1H), 7.26–7.16 (m, 4H), 6.47 (s, 1H), 3.45 (t, J = 7.4 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H), 1.96–1.93 (m, 1H), 1.06-1.02 (m, 2H), 0.90–0.84 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 210.0, 158.2, 140.8, 136.9, 129.3, 122.7, 121.9, 119.8, 117.1, 114.0, 106.0, 43.2, 23.9, 20.6, 10.8. **HRMS (ESI+)** calcd for $C_{18}H_{18}N_3O$, **[M+H]$^+$**: 292.1444, found: 292.1446.

*4.21. 1-Cyclohexyl-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)propan-1-one (**4e**) [21]*

Yield: 84%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (d, J = 4.8 Hz, 2H), 8.27 (d, J = 8.2 Hz, 1H), 7.53–7.51 (m, 1H), 7.26–7.13 (m, 3H), 6.45 (s, 1H), 3.39 (t, J = 7.2 Hz, 2H), 2.91 (t, J = 7.8 Hz, 2H), 2.39-2.31 (m, 1H), 1.85–1.75 (m, 4H), 1.36–1.20 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 213.2, 158.2, 141.0, 136.9, 129.3, 122.7, 121.9, 119.7, 117.1, 114.0, 106.0, 50.9, 40.5, 28.5, 25.7, 23.7. **HRMS (ESI+)** calcd for $C_{21}H_{24}N_3O$, **[M+H]$^+$**: 334.1914, found: 334.1916.

*4.22. 1-Phenyl-5-(1-(pyrimidin-2-yl)-1H-indol-2-yl)pentan-3-one (**4f**)*

Yield: 75%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (d, J = 4.8 Hz, 2H), 8.21 (d, J = 8.3 Hz, 1H), 7.44–7.41 (m, 1H), 7.20–7.03 (m, 8H), 6.34 (s, 1H), 3.34 (t, J = 6.9 Hz, 2H), 2.83–2.75 (m, 4H), 2.67 (t, J = 7.6 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 209.1, 158.2, 158.1, 141.1, 140.5, 136.9, 129.2, 128.5, 128.5, 128.4, 126.1, 122.8, 122.0, 119.8, 117.1, 114.1, 106.1, 44.4, 42.8, 29.8, 23.7. **HRMS (ESI+)** calcd for $C_{23}H_{22}N_3O$, **[M+H]$^+$**: 356.1757, found: 356.1759.

*4.23. 1-Phenyl-4-(1-(pyrimidin-2-yl)-1H-indol-2-yl)butan-2-one (**4g**) [22]*

Yield: 72%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (d, J = 4.8 Hz, 2H), 8.27 (d, J = 8.3 Hz, 1H), 7.50–7.48 (m, 1H), 7.31–7.10 (m, 8H), 6.37 (s, 1H), 3.70 (s, 2H), 3.39 (t, J = 7.0 Hz, 2H), 2.93 (t, J = 7.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.5, 158.1, 140.4, 136.9, 134.2, 129.4, 129.2, 128.8, 127.0, 122.8, 121.9, 119.8, 117.0, 114.1, 106.1, 50.3, 41.9, 23.7. **HRMS (ESI+)** calcd for $C_{22}H_{20}N_3O$, **[M+H]$^+$**: 342.1601, found: 342.1603.

*4.24. 1-Phenyl-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)propan-1-one (**4h**) [21]*

Yield: 70%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (d, J = 4.8 Hz, 2H), 8.31 (d, J = 8.4 Hz, 1H), 8.00–7.98 (m, 2H), 7.59-7.52 (m, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.24–7.13 (m, 3H), 6.53 (s, 1H), 3.61-3.57 (m, 2H), 3.49-3.45 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.3, 158.2, 140.9, 136.9, 133.1, 129.3, 128.6, 122.8, 128.0, 122.8, 122.0, 119.8, 117.1, 114.1, 106.2, 38.9, 24.2. **HRMS (ESI+)** calcd for $C_{21}H_{18}N_3O$, **[M+H]$^+$**: 328.1444, found: 328.1446.

*4.25. 3-(1-(Pyrimidin-2-yl)-1H-indol-2-yl)-1-(p-tolyl)propan-1-one (**4i**)*

Yield: 80%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (d, J = 4.8 Hz, 2H), 8.31 (t, J = 8.4 Hz, 1H), 7.89 (t, J = 8.2 Hz, 1H),7.54-7.52 (m, 1H), 7.28–7.17 (m, 5H), 6.53 (s, 1H), 3.58 (t, J = 4.8 Hz, 2H), 3.43 (t, J = 4.8 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.0, 158.3, 158.2, 143.9, 141.0, 136.9, 134.4, 129.3, 129.3, 128.2, 122.8, 122.0, 119.7, 117.1, 114.1, 106.2, 38.7, 24.2, 21.7. **HRMS (ESI+)** calcd for $C_{22}H_{20}N_3O$, **[M+H]$^+$**: 342.1601, found: 342.1603.

*4.26. 1-(4-Isopropylphenyl)-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl) propan-1-one (**4j**)*

Yield: 85%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 (d, J = 4.8 Hz, 2H), 8.30 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.54–7.52 (m, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.23–7.13 (m, 3H), 6.53 (s, 1H), 3.60–3.56 (m, 2H), 3.46–3.42 (m, 2H), 3.00-1.92 (m, 1H), 1.26 (d, J = 7.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.0, 158.3, 158.2, 154.6, 141.0, 136.9, 134.8, 129.3, 128.4, 126.7, 122.8, 121.9, 119.8, 117.1, 114.1, 106.2, 38.8, 34.3, 24.2, 23.7. **HRMS (ESI+)** calcd for $C_{24}H_{24}N_3O$, **[M+H]$^+$**: 370.1914, found: 370.1916.

*4.27. 1-(3-Chlorophenyl)-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl) propan-1-one (**4k**)*

Yield: 82%; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (d, J = 4.8 Hz, 2H), 8.32 (t, J = 7.6 Hz, 1H), 7.96 (s, 1H), 7.87–7.84 (m, 1H), 7.55–7.52 (m, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.26–7.14 (m, 3H), 6.53 (s 1H), 3.58 (t, J = 6.9 Hz, 2H), 3.47–3.43 (m 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.1, 158.3, 158.2, 140.5, 138.4, 136.9, 135.0, 133.0, 130.0, 129.2, 128.1, 126.2, 122.9, 122.0, 119.9, 117.1, 114.2, 106.4, 39.2, 24.2. **HRMS (ESI+)** calcd for $C_{21}H_{17}ClN_3O$, **[M+H]$^+$**: 362.1055, found: 362.1057.

4.28. Procedure for reusing of Rh(III)/H_2O catalytic system

1-(pyrimidin-2-yl)-1H-indole **1a** (0.2 mmol, 1.0 equiv), but-3-en-2-ol **2a** (0.4 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), H_2O (2.0 mL) were charged into Schlenk tube under air. The reaction mixture was stirred for 12 h at 80 °C. After the reaction was complete, the mixture was cooled to room temperature and the reaction mixture was extracted with ethyl acetate (3*10 mL), the organic phase was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (5:1) to afford the product **3a** in 92% yield. And the resulting water phase containing the Rh(III) catalyst was recharged with fresh substrates of 1-(pyrimidin-2-yl)-1H-indole (**1a,** 0.2 mmol) and but-3-en-2-ol (**2a,** 0.4 mmol) for the next run, this operation was repeated for five cycles, and the yield was obtained in 90%, 88%, 86%, 85% and 55%, respectively.

Notes

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2018.10.074.

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