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Rhodium(III)-Catalyzed Mild Alkylation of (Hetero)Arenes with Cyclopropanols via C−H Activation and Ring Opening

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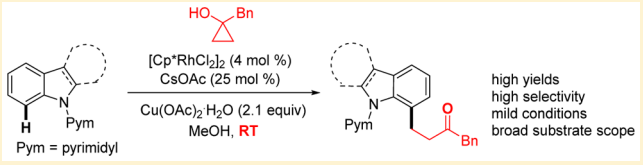
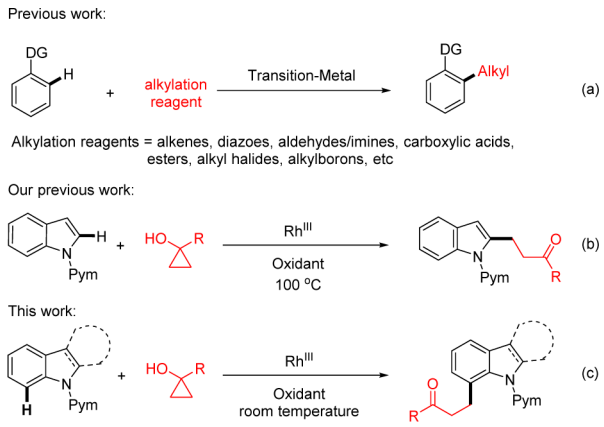
Supporting Information

ABSTRACT: The rhodium(III)-catalyzed regioselective alkylation of (hetero)arenes using cyclopropanols as a reactive and efficient coupling partner under oxidative conditions has been developed. This coupling occurred at room temperature via C−H activation of arenes and C−C cleavage of cyclopropanols. Various types of (hetero)arenes (indolines, carbazole, tetrahydrocarbazole, pyrrole, thiophene, etc.) were all successfully reacted under the present conditions. This protocol provides the facile and efficient construction of C7-alkylated indoline scaffolds.



The ubiquity of C−C(alkyl) bonds in natural products and commercial drugs has inspired the development of simple, efficient, and economical approaches to forge C−C(alkyl) bonds.[1] Over the past decades, transition-metal-catalyzed C−H activation has emerged as a promising strategy to achieve this process.[2] In this context, various conventional coupling partners such as alkenes,[3] diazo compounds,[4] aldehydes/imines,[5] carboxylic acids/esters,[6] alkyl halides,[7] and organoboron reagents[8] have been applied as alkylating reagents (Scheme 1a). Despite the abundant selections of coupling partners, it is necessary to further explore new alkylating reagents to meet the challenge of diverse synthesis. Strained rings are generally reactive, and coupling using such rings opened more avenues for the formation of various C−C bonds.[9] In particular, cyclopropanols as readily available strained rings have been widely employed in synthesis of natural products,[10] and ring-opening couplings of cyclopropanols provided access to synthetically important β-functionalized ketones in the presence of a transition-metal catalyst or a radical initiator.[11]

Scheme 1. Direct C−H Alkylation of Arenes



Although diversely synthetic approaches utilizing cyclopropanols have been developed, very few reports combined C−H activation of arenes with ring opening of cyclopropanols.[11b,12]

Rhodium(III) catalysts are particularly efficient in C−H activation of arenes.[13] Recently, we reported a Rh(III)-catalyzed coupling of *N*-pyrimidylindoles with cyclopropanols via C−H activation (Scheme 1b).[12] Given the potential of this synthetic method, we expect to further explore usage of cyclopropanols. On the other hand, indoles and indolines have been identified as important skeletons in numerous natural compounds and pharmaceuticals.[14] Consequently, synthetic methods to access functionalized indoles and indolines have been extensively studied over the past decades.[15] To date, selective C−H alkylations of indoles and indolines at the 7-position have limited precedents.[3f,4d,6e,16] As a continuation of our interest in C−H activation, we now report the selective alkylation of indolines with cyclopropanols under mild conditions (Scheme 1c).

We began our investigation using *N*-pyrimidylindoline (**1a**) and 1-benzylcyclopropanol (**2a**) as model substrates. The coupling of **1a** and **2a** was initially performed in the presence of $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), and $Cu(OAc)_2 \cdot H_2O$ (2.1 equiv) in methanol (100 °C). To our delight, the corresponding coupling product **3aa** was isolated in 51% yield (Table 1, entry **1**). Switching to $[Cp^*Rh(OAc)_2]$ as a catalyst afforded a slightly lower yield (entry **2**). Further optimization by lowering the reaction temperature improved the reaction efficiency, and the isolated yield of **3aa** was improved to 85% when the reaction was performed at room temperature. Changing the solvent (DCE or TFE) gave inferior results. Our control experiment indicated that no desired product was detected in the absence of a rhodium catalyst.

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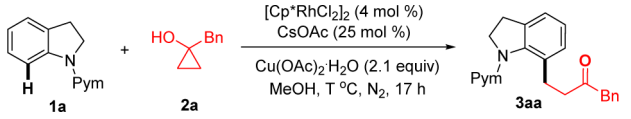
Table 1. Optimization Studies[a]

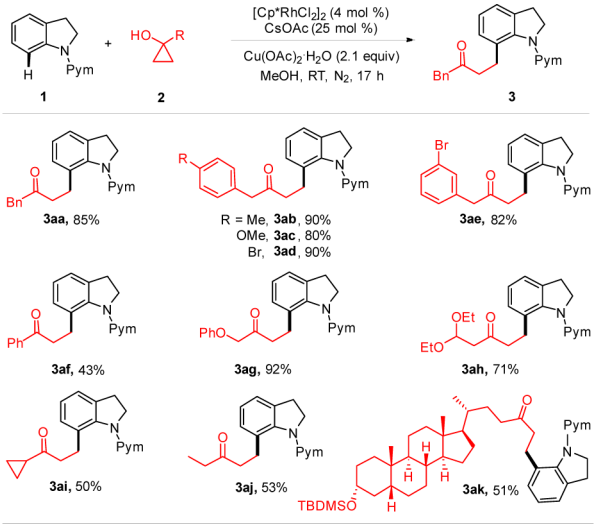


entry	catalyst	temp (°C)	yield (%)[b]
1	$[Cp^*RhCl_2]_2$	100	51
2[c]	$[Cp^*Rh(OAc)_2]$	100	42
3	$[Cp^*RhCl_2]_2$	80	60
4	$[Cp^*RhCl_2]_2$	60	70
5	$[Cp^*RhCl_2]_2$	40	72
6	$[Cp^*RhCl_2]_2$	25	85
7[d]	$[Cp^*RhCl_2]_2$	25	51
8[e]	$[Cp^*RhCl_2]_2$	25	75
9		25	NR[f]

[a]Reaction conditions: $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2·H_2O$ (2.1 equiv), **1a** (0.2 mmol), and **2a** (0.25 mmol) in a solvent (2 mL) for 17 h. [b]Isolated yield after column chromatography. [c]$[Cp^*Rh(OAc)_2]$ (8 mol %) was used as a catalyst. [d]DCE (1,2-dichloroethane, 2 mL) was used as a solvent. [e]TFE (2,2,2-trifluoroethanol, 2 mL) was used as a solvent. [f]No reaction.

With the optimal conditions established, the scope of cyclopropanols was next investigated using **1a** (Scheme 2). 1-

Scheme 2. Substrate Scope for Cyclopropanols[a,b]

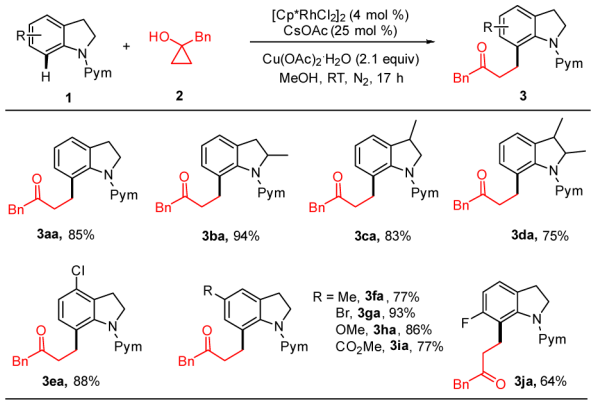


[a]Reaction conditions: $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2·H_2O$ (2.1 equiv), **1a** (0.2 mmol), and **2** (0.25 mmol) in MeOH (2 mL) at room temperature for 17 h. [b]Isolated yield after column chromatography.

Benzylcyclopropanols with electron-donating and electron-withdrawing substitutions at the *para*-position of the benzene ring all gave excellent yields (**3aa**–**3ad**). Introduction of a *m*-Br was well-tolerated and the product (**3ae**) was obtained in 82% yield. While phenyl-substituted cyclopropanols (**2f**) underwent desired coupling in a slightly lower yield, phenoxyl (**3ag**), acetal (**3ah**), and alkyl (cyclopropyl, **3ai**; ethyl, **3aj**) substrates all gave smooth coupling. Notably, a natural product-derived cyclopropanol was also viable, which provided an efficient method to functionalize complex molecules.

We next explored the generality with respect to *N*-pyrimidinylindolines (Scheme 3). In all cases, various

Scheme 3. Substrate Scope for Indolines[a,b]

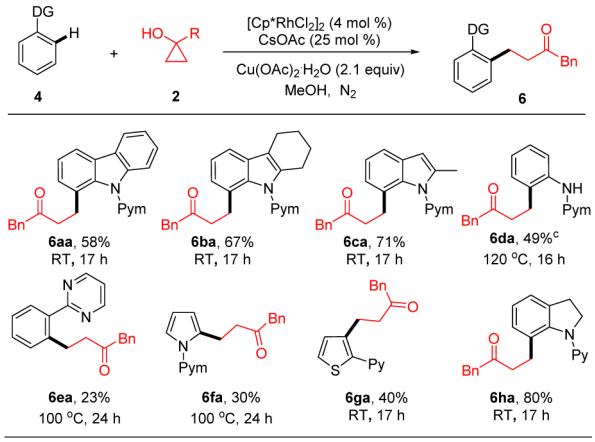


[a]Reactions were carried out by using $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2·H_2O$ (2.1 equiv), **1** (0.2 mmol), and **2a** (0.25 mmol) in MeOH (2 mL) at room temperature for 17 h. [b]Isolated yield after column chromatography.

substituted indolines reacted smoothly to give the desired product in good to excellent yields. The introduction of methyl or dimethyl groups into the indoline skeleton afforded the corresponding products (**3ba**, **3ca**, and **3da**) in 75–94% yields. In addition, indolines bearing different electron-withdrawing groups at the C4–C6 positions were all tolerated (**3ea**–**3ja**).

The arene substrate was not restricted to an indoline (Scheme 4). The coupling of a carbazole or a tetrahydrocarba-

Scheme 4. Substrate Scope of Other Arenes[a,b]



[a]Reactions were carried out by using $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2·H_2O$ (2.1 equiv), **4** (0.2 mmol), and **2a** (0.25 mmol) in MeOH (2 mL). [b]Isolated yield after column chromatography. [c]Reaction was carried out using $[Rh(OAc)_2]$ (4 mol %), $Cu(OAc)_2·H_2O$ (2.1 equiv), **4** (0.2 mmol), and **2a** (0.25 mmol) in MeOH (2 mL).

zole with cyclopropanol **2a** delivered the alkylation product **6aa** or **6ba** in moderate yields. Furthermore, arene substrates were extended to indole **6ca**, aniline **6da**, 2-phenylpyrimidine **6ea**, pyrrole **6fa**, and thiophene **6ga**. In all cases, reactions proceeded smoothly under the standard or slightly modified conditions.

To demonstrate the synthetic applicability of this protocol, a gram-scale synthesis of **3aa** was conducted, which was obtained in 85% yield at a reduced catalyst loading (2 mol %), demonstrating that the reaction is scalable (eq 1). Treatment of

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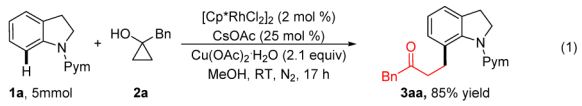
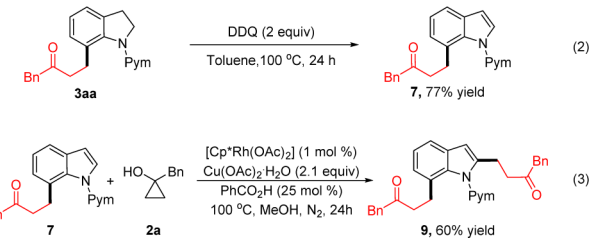


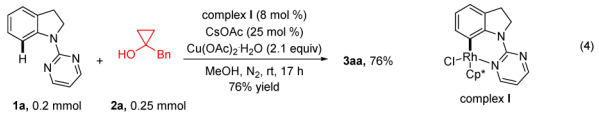
(1)

3aa with DDQ led to the C7-alkylated indole, which provides a new route to access such an alkylated indole (eq 2). Moreover, the product **7** could be further alkylated at the C2-position to afford a dialkylation product (**9**) on the basis of our previous report (eq 3).[12]



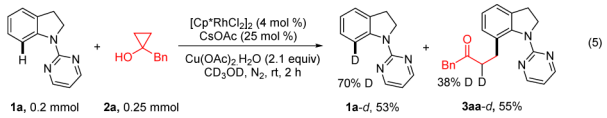
(2) (3)

A series of experiments have been conducted to probe the reaction mechanism. Cyclometalated rhodium complex **I** was designated as a catalyst precursor (8 mol %) under the standard conditions, and the desired product (**3aa**) was isolated in 76% yield (eq 4), which suggested the relevancy of C−H activation.



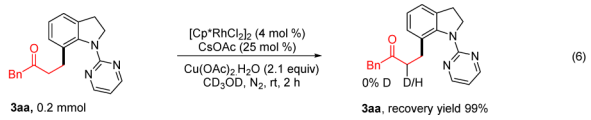
(4)

Coupling of **1a** with **2a** under the standard conditions in CD_3OD provided **3aa**-*d* with recovery of **1a**-*d* and formation of **3aa**-*d* (eq 5), indicating the reversible C−H activation at the



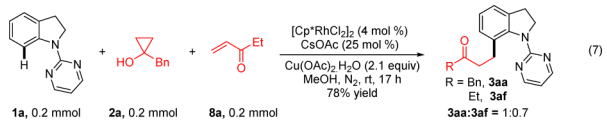
(5)

C7-position of **1a**. A control experiment confirmed that the deuterium incorporation in product **3aa**-*d* did not result from postcoupling H/D exchange (eq 6). On the other hand, when



(6)

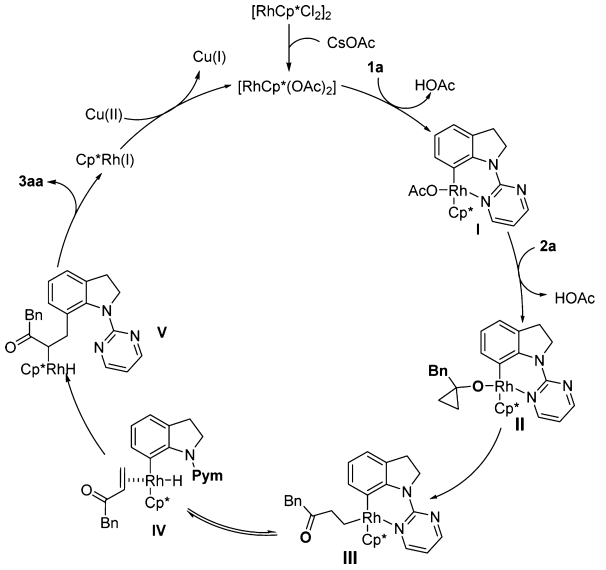
ethyl vinyl ketone (EVK, 1.0 equiv) was introduced into the reaction system, a mixture of **3aa** and **3af** (eq 7) was obtained, indicating that an olefin species is likely involved as an intermediate.



(7)

On the basis of our preliminarily mechanistic studies and previous work,[12] a plausible mechanism is given in Scheme 5. The reaction starts from formation of $[Cp^*Rh(OAc)_2]$ via ligand substitution, which subsequently reacts with **1a** via C−H activation to form the intermediate **I**. **I** then undergoes ligand exchange with cyclopropanol to form the Rh(III) alkoxide **II**. *β*-

Scheme 5. Proposed Mechanism



Carbon elimination of **II** affords a homoenolate species **III** that then undergoes reversible *β*-H elimination. Subsequently, migratory insertion of the Rh−C bond in **IV** into the olefin unit generates intermediate **V**, which then undergoes C−H reductive elimination to release the product **3aa** and Rh(I). The Rh(I) species is then reoxidized by Cu(II) to the active Rh(III) catalyst. The observed deuterium incorporation at the *α*-position of product **3aa**-*d*, when CD_3OD was used, seems consistent with this mechanism because H/D exchange can readily occur for a Rh(III) hydride/deuteride species. However, direct reductive elimination of **III** to **3aa** and Rh(I) cannot be completely ruled out, although our previous studies indicated that this was unlikely in the ring-opening coupling between *N*-pyrimidylindole and cyclopropanol.[12]

In summary, we have developed an efficient rhodium-catalyzed direct alkylation of various (hetero)arenes with cyclopropanol via a sequence of C−H activation and ring opening, leading to synthesis of a series of *β*-aryl ketones. The catalytic reaction proceeded under mild conditions with good efficiency, broad substrate scope, and excellent functional group compatibility. Owing to the importance of *β*-aryl ketone compounds in synthetic chemistry, this protocol is expected to find applications in the synthesis of related complex structures.

EXPERIMENTAL SECTION

General Information. All chemicals were obtained from commercial suppliers and were used as received unless otherwise noted. Substituted indolines,[17] *N*-pyrimidinylindoline,[6e] *N*-acetylindoline,[18] *N*,*N*-diethylcarbamylindoline,[18] *N*-(2-pyridinyl)indoline,[19] cyclopropanols,[12] *N*-pyrimidinylcarbazole,[20] *N*-pyrimidinylaniline,[21] *N*-pyrimidinylpyrole,[20] *N*-pyrimidinylindole,[20] and 2-pyrimidinylbenzene[22] were prepared according to the previously reported synthetic method. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ as a solvent on a 400 MHz NMR spectrometer. The chemical shift is given in dimensionless δ values and is referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. All coupling constants (J values) were reported in hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). HRMS data were obtained via ESI mode with a TOF mass analyzer. Column chromatography was performed on silica gel (300−400 mesh) with freshly distilled ethyl acetate (EA) and petroleum ether (PE).

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Typical Experimental Procedure for Rh(III)-Catalyzed Selective C−H Activation of Arenes To Construct C−C(Alkyl) Bonds. *N*-Pyrimidinylindoline (**1a**, 0.2 mmol), 1-benzylcyclopropanol (**2a**, 0.25 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), CsOAc (25 mol %), $Cu(OAc)_2 \cdot H_2O$ (2.1 equiv), and methanol (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at room temperature for 17 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford compound (**3aa**, 58 mg, 85% yield).

1-Phenyl-4-(1-(pyrimidin-2-yl)indolin-7-yl)butan-2-one (***3aa***). Yellow solid (58 mg, 85%); mp 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 4.8 Hz, 2H), 7.36−7.25 (m, 3H), 7.20−7.10 (m, 3H), 7.09−7.00 (m, 2H), 6.66 (t, J = 4.8 Hz, 1H), 4.42 (t, J = 7.7 Hz, 2H), 3.63 (s, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.93−2.87 (m, 2H), 2.87−2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 161.3, 157.7, 142.5, 135.2, 134.5, 131.1, 129.5, 128.8, 128.3, 127.0, 124.5, 122.6, 112.5, 53.3, 50.2, 41.6, 29.9, 28.1; HRMS $[M + H]^+$ calcd for $C_{22}H_{22}N_3O$ 344.1763, found 344.1763.

4-(1-(Pyrimidin-2-yl)indolin-7-yl)-1-(p-tolyl)butan-2-one (***3ab***). Yellow oil (64 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 4.8 Hz, 2H), 7.16−7.08 (m, 3H), 7.07−6.98 (m, 4H), 6.63 (t, J = 4.8 Hz, 1H), 4.40 (t, J = 7.7 Hz, 2H), 3.57 (s, 2H), 3.03 (t, J = 7.6 Hz, 2H), 2.90−2.84 (m, 2H), 2.84−2.76 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 161.2, 157.6, 142.4, 136.5, 135.1, 131.3, 131.1, 129.4, 129.3, 128.3, 124.4, 122.5, 112.4, 53.2, 49.8, 41.4, 29.9, 28.0, 21.1; HRMS $[M + H]^+$ calcd for $C_{23}H_{24}N_3O$ 358.1919, found 358.1920.

1-(4-Methoxyphenyl)-4-(1-(pyrimidin-2-yl)indolin-7-yl)butan-2-one (***3ac***). Yellow oil (59.7 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 4.8 Hz, 2H), 7.13−7.08 (dd, J = 5.8, 2.5 Hz, 1H), 7.07−6.97 (m, 4H), 6.83 (d, J = 8.6 Hz, 2H), 6.63 (t, J = 4.8 Hz, 1H), 4.39 (t, J = 7.7 Hz, 2H), 3.79 (s, 3H), 3.53 (s, 2H), 3.02 (t, J = 7.6 Hz, 2H), 2.91−2.83 (m, 2H), 2.82−2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 161.2, 158.6, 157.6, 142.4, 135.2, 131.1, 130.4, 128.3, 126.4, 124.4, 122.5, 114.2, 112.4, 55.3, 53.3, 49.2, 41.4, 29.9, 28.1; HRMS $[M + H]^+$ calcd for $C_{23}H_{24}N_3O_2$ 374.1869, found 374.1869.

1-(4-Bomophenyl)-4-(1-(pyrimidin-2-yl)indolin-7-yl)butan-2-one (***3ad***). Yellow oil (76 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 4.8 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.14−7.09 (m, 1H), 7.04−6.99 (m, 2H), 6.97 (d, J = 8.3 Hz, 2H), 6.65 (t, J = 4.8 Hz, 1H), 4.38 (t, J = 7.7 Hz, 2H), 3.53 (s, 2H), 3.02 (t, J = 7.6 Hz, 2H), 2.89 (t, J = 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 161.2, 157.6, 142.4, 135.2, 133.2, 131.8, 131.1, 130.8, 128.3, 124.5, 122.6, 121.0, 112.5, 53.3, 49.3, 41.6, 29.9, 28.2; HRMS $[M + H]^+$ calcd for $C_{22}H_{21}BrN_3O$ 422.0868, found 422.0870.

1-(3-Bromophenyl)-4-(1-(pyrimidin-2-yl)indolin-7-yl)butan-2-one (***3ae***). Yellow oil (69 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 4.8 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.28−7.24 (m, 1H), 7.18−7.10 (m, 2H), 7.05−6.99 (m, 3H), 6.65 (t, J = 4.8 Hz, 1H), 4.39 (t, J = 7.6 Hz, 2H), 3.54 (s, 2H), 3.02 (t, J = 7.6 Hz, 2H), 2.91−2.85 (m, 2H), 2.81−2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 161.3, 157.7, 142.4, 136.5, 135.3, 132.4, 130.8, 130.2, 130.2, 129.5, 128.3, 128.2, 124.5, 122.7, 112.5, 53.3, 49.4, 41.8, 29.9, 28.1; HRMS $[M + H]^+$ calcd for $C_{22}H_{21}BrN_3O$ 422.0870, found 422.0868.

1-Phenyl-3-(1-(pyrimidin-2-yl)indolin-7-yl)propan-1-one (***3af***). Yellow oil (28 mg, 43%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 4.8 Hz, 2H), 7.97−7.83 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.20−7.11 (m, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.65 (t, J = 4.8 Hz, 1H), 4.43 (t, J = 7.7 Hz, 2H), 3.38−3.24 (m, 2H), 3.13−2.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 161.4, 157.7, 142.6, 137.0, 135.3, 133.0, 131.5, 128.6, 128.5, 128.1, 124.6, 122.7, 112.5, 53.4, 38.5, 30.0, 28.7; HRMS $[M + H]^+$ calcd for $C_{21}H_{20}N_3O$ 330.1606, found 330.1607.

1-Phenoxy-4-(1-(pyrimidin-2-yl)indolin-7-yl)butan-2-one (***3ag***). Yellow oil (66.3 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 4.8 Hz, 2H), 7.29−7.21 (m, 2H), 7.11 (d, J = 6.9 Hz, 1H), 7.06 (d, J = 6.9 Hz, 1H), 7.04−6.99 (m, 1H), 6.96 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 8.0 Hz, 2H), 6.65 (t, J = 4.8 Hz, 1H), 4.45 (s, 2H), 4.39 (t, J = 7.6 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H), 2.96−2.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 161.3, 157.8, 157.7, 142.5, 135.3, 130.8, 129.7, 128.3, 124.6, 122.7, 121.6, 114.5, 112.5, 72.8, 53.3, 38.7, 29.9, 27.6; HRMS $[M + H]^+$ calcd for $C_{22}H_{22}N_3O_2$ 360.1712, found 360.1711.

1,1-Diethoxy-5-(1-(pyrimidin-2-yl)indolin-7-yl)pentan-3-one (***3ah***). Yellow oil (52.6 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 4.8 Hz, 2H), 7.11 (d, J = 6.9 Hz, 1H), 7.08−6.98 (m, 2H), 6.68 (t, J = 4.8 Hz, 1H), 4.87 (t, J = 5.7 Hz, 1H), 4.42 (t, J = 7.6 Hz, 2H), 3.68−3.56 (m, 2H), 3.53−3.42 (m, 2H), 3.03 (t, J = 7.6 Hz, 2H), 2.91−2.83 (m, 2H), 2.83−2.73 (m, 2H), 2.66 (d, J = 5.7 Hz, 2H), 1.16 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 161.4, 157.7, 142.5, 135.2, 131.2, 128.2, 124.5, 122.5, 112.4, 99.9, 62.3, 53.3, 47.5, 43.7, 29.9, 27.7, 15.3; HRMS $[M + H]^+$ calcd for $C_{21}H_{28}N_3O_3$ 370.2131, found 370.2128.

1-Cyclopropyl-3-(1-(pyrimidin-2-yl)indolin-7-yl)propan-1-one (***3ai***). Yellow oil (29 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 4.8 Hz, 2H), 7.15−7.05 (m, 2H), 7.05−6.98 (m, 1H), 6.69 (t, J = 4.8 Hz, 1H), 4.43 (t, J = 7.4 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H), 2.96−2.90 (m, 2H), 2.90−2.82 (m, 2H), 1.86−1.78 (m, 1H), 0.97−0.90 (m, 2H), 0.82−0.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 161.4, 157.7, 142.5, 135.2, 131.4, 128.3, 124.5, 122.5, 112.5, 53.4, 43.0, 30.0, 28.4, 20.4, 10.6; HRMS $[M + H]^+$ calcd for $C_{18}H_{20}N_3O$ 294.1606, found 294.1606.

1-(1-(Pyrimidin-2-yl)indolin-7-yl)pentan-3-one (***3aj***). Yellow oil (30 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 4.8 Hz, 2H), 7.11 (d, J = 6.8 Hz, 1H), 7.08−6.98 (m, 1H), 6.69 (t, J = 4.8 Hz, 1H), 4.42 (t, J = 7.4 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.70 (t, J = 7.6 Hz, 2H), 2.31 (q, J = 7.1 Hz, 2H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 161.4, 157.7, 142.5, 135.2, 131.3, 128.3, 124.5, 122.6, 112.5, 53.4, 41.8, 35.9, 30.0, 28.4, 7.9; HRMS $[M + H]^+$ calcd for $C_{17}H_{20}N_3O$ 282.1606, found 282.1608.

(R)-6-((3R,5R,8R,9S,10S,13R,14S,17R)-3-((tert-Butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-1-(1-(pyrimidin-2-yl)indolin-7-yl)heptan-3-one (***3ak***). Pink solid (71 mg, 51%); mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 4.8 Hz, 2H), 7.11 (d, J = 7.0 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 7.03−6.99 (m, 1H), 6.69 (t, J = 4.8 Hz, 1H), 4.42 (t, J = 7.6 Hz, 2H), 3.66−3.51 (m, 1H), 3.04 (t, J = 7.7 Hz, 2H), 2.90 (t, J = 7.7 Hz, 2H), 2.74−2.65 (m, 2H), 2.37−2.25 (m, 1H), 2.25−2.13 (m, 1H), 1.91 (d, J = 11.9 Hz, 1H), 1.85−1.71 (m, 4H), 1.68−1.49 (m, 3H), 1.40−0.98 (m, 17H), 0.89 (s, 13H), 0.82 (d, J = 6.5 Hz, 3H), 0.60 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 161.4, 157.7, 142.5, 135.2, 131.3, 128.3, 124.5, 122.6, 112.5, 72.9, 56.5, 56.1, 53.4, 42.8, 42.4, 42.2, 40.3, 40.2, 39.7, 37.0, 36.0, 35.7, 35.4, 34.7, 31.1, 30.0, 28.4, 28.3, 27.4, 27.0, 26.5, 26.1, 24.3, 23.5, 20.9, 18.5, 18.4, 12.1, −4.5; HRMS $[M + H]^+$ calcd for $C_{44}H_{68}N_3O_2Si$ 698.5081, found 698.5082.

4-(2-Methyl-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (***3ba***). Yellow solid (67 mg, 94%); mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 4.7 Hz, 2H), 7.34−7.18 (m, 3H), 7.14−7.05 (m, 3H), 7.04−6.94 (m, 2H), 6.59 (t, J = 4.7 Hz, 1H), 5.09−4.89 (m, 1H), 3.56 (s, 2H), 3.44−3.34 (m, 1H), 3.03−2.91 (m, 1H), 2.84−2.66 (m, 3H), 2.45 (d, J = 15.4 Hz, 1H), 1.31 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 160.7, 157.6, 140.7, 134.4, 133.8, 131.3, 129.4, 128.7, 128.4, 127.0, 124.4, 123.1, 112.4, 60.3, 50.2, 41.4, 36.8, 28.2, 21.1; HRMS $[M + H]^+$ calcd for $C_{23}H_{24}N_3O$ 358.1919, found 358.1919.

4-(3-Methyl-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (***3ca***). Yellow solid (59.3 mg, 83%); mp 91−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 4.8 Hz, 2H), 7.33−7.23 (m, 3H), 7.16−7.10 (m, 2H), 7.08−6.98 (m, 3H), 6.61 (t, J = 4.8 Hz, 1H), 4.59 (dd, J = 11.0, 7.7 Hz, 1H), 3.85 (dd, J = 11.0, 7.7 Hz, 1H), 3.60 (s, 2H), 3.40−3.28 (m, 1H), 2.93−2.71 (m, 4H), 1.25 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 161.5, 157.8, 142.2, 140.4, 134.5, 131.1, 129.5, 128.8, 128.4, 127.1, 124.7, 121.3, 112.4, 61.1, 50.2, 41.7, 36.5, 28.0, 18.5; HRMS $[M + H]^+$ calcd for $C_{23}H_{24}N_3O$ 358.1919, found 358.1919.

4-(2,3-Dimethyl-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (***3da***). Yellow solid (55.3 mg, 75%); mp 55−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 4.8 Hz, 2H), 7.33−7.19 (m, 3H), 7.15−6.95 (m, 5H), 6.60 (t, J = 4.8 Hz, 1H), 4.54 (q, J = 6.5 Hz, 1H), 3.56 (s, 2H), 3.02−2.90 (m, 1H), 2.85−2.60 (m, 4H), 1.31 (d, J = 6.6

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J. Org. Chem. 2016, 81, 4869−4875

Hz, 3H), 1.12 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 161.5, 157.8, 140.0, 139.3, 134.5, 131.3, 129.4, 128.8, 128.6, 127.0, 124.5, 122.5, 112.5, 68.1, 50.2, 44.1, 41.4, 28.2, 21.5, 20.6; HRMS [M + H]$^+$ calcd for $C_{24}H_{26}N_3O$ 372.2076, found 372.2074.

*4-(4-Chloro-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (**3ea**).* Yellow solid (66 mg, 85%); mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 4.8 Hz, 2H), 7.33−7.21 (m, 3H), 7.10 (d, J = 6.9 Hz, 2H), 7.00−6.95 (m, 2H), 6.65 (t, J = 4.8 Hz, 1H), 4.37 (t, J = 7.8 Hz, 2H), 3.58 (s, 2H), 3.03 (t, J = 7.8 Hz, 2H), 2.84−2.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 161.0, 157.7, 143.6, 134.2, 133.3, 129.8, 129.4, 129.3, 128.8, 128.1, 127.0, 124.2, 112.9, 52.9, 50.2, 41.3, 29.2, 27.6; HRMS [M + H]$^+$ calcd for $C_{22}H_{21}ClN_3O$ 378.1373, found 378.1370.

*4-(5-Methyl-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (**3fa**).* Yellow solid (55 mg, 77%); mp 111−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 4.8 Hz, 2H), 7.34−7.20 (m, 3H), 7.15−7.09 (m, 2H), 6.91 (s, 1H), 6.81 (s, 1H), 6.58 (t, J = 4.8 Hz, 1H), 4.36 (t, J = 7.6 Hz, 2H), 3.59 (s, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.86−2.75 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 161.5, 157.6, 140.2, 135.4, 134.5, 134.2, 130.8, 129.5, 128.8, 128.8, 127.0, 123.4, 112.2, 53.4, 50.2, 41.7, 29.9, 28.0, 21.1; HRMS [M + H]$^+$ calcd for $C_{23}H_{24}N_3O$ 358.1919, found 358.1920.

*4-(5-Bromo-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (**3ga**).* Yellow solid (78 mg, 93%); mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 4.8 Hz, 2H), 7.33−7.23 (m, 3H), 7.19 (s, 1H), 7.16−7.09 (m, 3H), 6.63 (t, J = 4.8 Hz, 1H), 4.36 (t, J = 7.7 Hz, 2H), 3.60 (s, 2H), 2.97 (t, J = 7.7 Hz, 2H), 2.82−2.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 161.0, 157.6, 141.8, 137.4, 134.2, 132.9, 130.8, 129.4, 128.8, 127.0, 125.5, 116.9, 112.8, 53.3, 50.2, 41.2, 29.6, 27.7; HRMS [M + H]$^+$ calcd for $C_{22}H_{21}BrN_3O$ 422.0868, found 422.0870.

*4-(5-Methoxy-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (**3ha**).* Brown oil (64 mg, 86%); mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 4.8 Hz, 2H), 7.34−7.20 (m, 3H), 7.12 (d, J = 6.8 Hz, 2H), 6.68 (d, J = 2.4 Hz, 1H), 6.58 (t, J = 4.8 Hz, 1H), 6.55 (d, J = 2.4 Hz, 1H), 4.37 (t, J = 7.5 Hz, 2H), 3.75 (s, 3H), 3.59 (s, 2H), 2.96 (t, J = 7.5 Hz, 2H), 2.87−2.76 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 161.5, 157.6, 157.1, 136.7, 136.0, 134.4, 132.2, 129.4, 128.8, 127.0, 113.1, 112.1, 108.7, 55.7, 53.5, 50.2, 41.6, 30.3, 28.1; HRMS [M + H]$^+$ calcd for $C_{23}H_{24}N_3O_2$ 374.1869, found 374.1870.

*Methyl 7-(3-Oxo-4-phenylbutyl)-1-(pyrimidin-2-yl)indoline-5-carboxylate (**3ia**).* Yellow solid (62 mg, 77%); mp 108−109 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.25 (d, J = 4.8 Hz, 2H), 7.75 (d, J = 2.7 Hz, 2H), 7.38−7.19 (m, 3H), 7.17−7.08 (m, 2H), 6.67 (t, J = 4.8 Hz, 1H), 4.39 (t, J = 7.9 Hz, 2H), 3.88 (s, 3H), 3.61 (s, 2H), 3.05 (t, J = 7.8 Hz, 2H), 2.87−2.97 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 207.5, 167.0, 160.7, 157.6, 146.6, 135.3, 134.3, 130.8, 130.0, 129.4, 128.8, 127.0, 125.7, 123.8, 113.2, 53.4, 52.0, 50.2, 41.4, 29.2, 27.9; HRMS [M + H]$^+$ calcd for $C_{24}H_{24}N_3O_3$ 402.1818, found 402.1821.

*4-(6-Fluoro-1-(pyrimidin-2-yl)indolin-7-yl)-1-phenylbutan-2-one (**3ja**).* White solid (46 mg, 64%); mp 44−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 4.8 Hz, 2H), 7.34−7.22 (m, 3H), 7.22−7.14 (m, 2H), 7.04−6.96(m, 1H), 6.75−6.67 (m, 1H), 6.57 (t, J = 4.8 Hz, 1H), 4.38 (t, J = 7.7 Hz, 2H), 3.63 (s, 2H), 3.02−2.90 (m, 4H), 2.74 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 161.7 (d, J_{C-F} = 241.4 Hz), 161.1, 157.6, 134.6, 130.4, 129.5, 128.8, 127.0, 122.7 (d, J_{C-F} = 11.1 Hz), 119.1 (d, J_{C-F} = 19.2 Hz), 112.9, 110.5 (d, J_{C-F} = 24.2 Hz),, 54.0, 50.2, 40.4, 29.3, 22.1; HRMS [M + H]$^+$ calcd for $C_{22}H_{21}FN_3O$ 362.1669, found 362.1669.

*1-Phenyl-4-(9-(pyrimidin-2-yl)-9H-carbazol-1-yl)butan-2-one (**6aa**).* Yellow oil (45 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 2H), 8.03 (d, J = 7.6 Hz, 1H), 8.01−7.92 (m, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.35−7.17 (m, 6H), 7.13−7.04 (m, 3H), 3.49 (s, 2H), 2.83 (t, J = 7.8 Hz, 2H), 2.68 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 158.8, 158.6, 141.4, 138.2, 134.2, 129.4, 128.8, 128.4, 127.1, 126.9, 126.8, 126.7, 125.5, 122.5, 122.1, 120.0, 118.4, 118.3, 112.4, 50.1, 41.7, 28.0; HRMS [M + H]$^+$ calcd for $C_{26}H_{22}N_3O$ 392.1763, found 392.1762.

*1-Phenyl-4-(9-(pyrimidin-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-8-yl)butan-2-one (**6ba**).* Yellow oil (53 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 4.8 Hz, 2H), 7.39−7.20 (m, 4H), 7.16−7.02 (m, 4H), 6.92 (d, J = 7.2 Hz, 1H), 3.48 (s, 2H), 2.76−2.53 (m, 8H), 1.90−1.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 158.6, 158.4, 137.0, 134.8, 134.3, 130.5, 129.5, 128.8, 127.1, 125.2, 124.2, 121.3, 118.6, 116.4, 113.8, 50.1, 42.5, 27.5, 23.8, 23.5, 22.8, 21.2; HRMS [M + H]$^+$ calcd for $C_{26}H_{26}N_3O$ 396.2076, found 396.2074.

*4-(2-Methyl-1-(pyrimidin-2-yl)-1H-indol-7-yl)-1-phenylbutan-2-one (**6ca**).* Brown oil (50.6 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 4.8 Hz, 2H), 7.40 (d, J = 7.7 Hz, 1H), 7.34−7.21 (m, 3H), 7.18−7.09 (m, 3H), 7.05 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.39 (s, 1H), 3.49 (s, 2H), 2.67−2.55 (m, 2H), 2.55−2.42 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 159.0, 158.6, 138.1, 135.6, 134.3, 130.3, 129.5, 128.8, 127.1, 124.6, 123.8, 121.4, 119.5, 118.4, 104.2, 50.1, 42.7, 26.9, 14.0; HRMS [M + H]$^+$ calcd for $C_{23}H_{22}N_3O$ 356.1763, found 356.1764.

*1-Phenyl-4-(2-(pyrimidin-2-ylamino)phenyl)butan-2-one (**6da**).* Brown solid (31.2 mg, 49%); mp 78−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 4.8 Hz, 2H), 7.91 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.30−7.19 (m, 4H), 7.14−7.07 (m, 3H), 7.06−7.02 (m, 1H), 6.64 (t, J = 4.8 Hz, 1H), 3.63 (s, 2H), 2.92−2.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 161.1, 158.3, 137.0, 134.0, 133.5, 129.8, 129.4, 128.8, 127.1, 127.0, 124.7, 124.2, 112.2, 50.2, 42.9, 24.8; HRMS [M + H]$^+$ calcd for $C_{20}H_{20}N_3O$ 318.1606, found 318.1607.

*1-Phenyl-4-(2-(pyrimidin-2-yl)phenyl)butan-2-one (**6ea**).* Brownish black oil (14 mg, 23%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.8 Hz, 2H), 7.86−7.78 (m, 1H), 7.37−7.23 (m, 6H), 7.21−7.12 (m, 3H), 3.64 (s, 2H), 3.11 (t, J = 7.8 Hz, 2H), 2.86 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 167.3, 157.0, 140.5, 137.9, 134.5, 131.0, 130.8, 129.9, 129.5, 128.8, 127.0, 126.6, 118.8, 50.3, 44.3, 28.3; HRMS [M + H]$^+$ calcd for $C_{20}H_{19}N_2O$ 303.1497, found 303.1497.

*1-Phenyl-4-(1-(pyrimidin-2-yl)-1H-pyrrol-2-yl)butan-2-one (**6fa**).* Brown oil (17 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 2H), 7.76−7.69 (m, 1H), 7.33−7.24 (m, 3H), 7.19 (d, J = 6.9 Hz, 2H), 7.01 (t, J = 4.8 Hz, 1H), 6.18 (t, J = 3.3 Hz, 1H), 6.04−5.96 (m, 1H), 3.69 (s, 2H), 3.33 (t, J = 7.6 Hz, 2H), 2.87 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 158.2, 134.5, 134.0, 129.6, 128.8, 127.1, 121.1, 117.0, 112.0, 110.0, 100.1, 50.4, 42.4, 24.1; HRMS [M + H]$^+$ calcd for $C_{18}H_{18}N_3O$ 292.1450, found 292.1451.

*1-Phenyl-4-(2-(pyridin-2-yl)thiophen-3-yl)butan-2-one (**6ga**).* Brown oil (24 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61−8.51 (m, 1H), 7.65 (td, J = 7.8, 1.9 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.34−7.21 (m, 4H), 7.21−7.10 (m, 3H), 6.89 (d, J = 5.1 Hz, 1H), 3.68 (s, 2H), 3.17 (t, J = 7.8 Hz, 2H), 2.84 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 153.4, 149.7, 139.2, 138.1, 136.7, 134.3, 130.8, 129.5, 128.85, 127.1, 125.8, 121.9, 121.6, 50.3, 42.7, 23.9; HRMS [M + H]$^+$ calcd for $C_{18}H_{16}NOS$ 294.0953, found 294.0952.

*1-Phenyl-4-(1-(pyridin-2-yl)indolin-7-yl)butan-2-one (**6ha**).* Brown oil (54.7 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 3.9 Hz, 1H), 7.54−7.43 (m, 1H), 7.33−7.16 (m, 3H), 7.14−7.04 (m, 3H), 6.98−6.90 (m, 2H), 6.80−6.72 (m, 1H), 6.63 (d, J = 8.3 Hz, 1H), 4.22 (t, J = 7.8 Hz, 2H), 3.52 (s, 2H), 3.02 (t, J = 7.8 Hz, 2H), 2.73−2.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 157.9, 147.7, 143.6, 137.5, 135.0, 134.2, 129.4, 129.0, 128.7, 128.4, 126.9, 123.6, 123.0, 115.9, 111.6, 55.3, 50.0, 41.2, 29.9, 27.4; HRMS [M + H]$^+$ calcd for $C_{23}H_{23}N_2O$ 343.1810, found 343.1811.

Derivatization of Indoline 3aa. To a solution of **3aa** (0.3 mmol) in toluene (3 mL) was added DDQ (0.6 mmol). The mixture was stirred at 100 °C for 24 h. The resulting mixture was cooled to room temperature, and then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford compound **7**.

*1-Phenyl-4-(1-(pyrimidin-2-yl)-1H-indol-7-yl)butan-2-one (**7**).* Brown oil (52.5 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.8 Hz, 2H), 7.80 (d, J = 3.6 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.32−7.23 (m, 3H), 7.16 (t, J = 7.5 Hz, 1H), 7.13−7.05 (m, 3H), 7.00 (t, J = 4.8 Hz, 1H), 6.69 (d, J = 3.6 Hz, 1H), 3.52 (s, 2H), 3.12 (t, J = 7.7 Hz, 2H), 2.73 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 158.4, 158.2, 134.4, 133.7, 132.5, 130.2, 129.5, 128.8,

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J. Org. Chem. 2016, 81, 4869−4875

127.3, 127.1, 125.9, 122.5, 119.5, 117.5, 107.2, 50.3, 42.7, 29.0; HRMS $[M + H]^+$ calcd for $C_{22}H_{20}N_3O$ 342.1606, found 342.1605.

Derivatization Reaction for Functionalization of Indole 7. C7-alkylation of *N*-pyrimidinylindoline (**7**, 0.2 mmol), 1-benzylcyclopropanol (**2a**, 0.25 mmol), $[Cp^*Rh(OAc)_2]$ (1 mol %), $PhCO_2H$ (25 mol %), $Cu(OAc)_2·H_2O$ (2.1 equiv), and methanol (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 100 °C for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford compound **9**.

*4,4′-(1-(Pyrimidin-2-yl)-1H-indole-2,7-diyl)bis(1-phenylbutan-2-one) (**9**).* Brown oil (58.4 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 4.8 Hz, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.34−7.24 (m, 6H), 7.19−7.09 (m, 5H), 7.05 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.2 Hz, 1H), 6.30 (s, 1H), 3.65 (s, 2H), 3.50 (s, 2H), 2.88−2.75 (m, 4H), 2.59 (t, J = 7.9 Hz, 2H), 2.43 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 207.0, 158.9, 158.7, 141.0, 135.8, 134.3, 134.2, 130.0, 129.5, 129.5, 128.9, 128.9, 127.2, 127.2, 124.8, 124.1, 121.5, 119.7, 118.6, 103.4, 50.3, 50.2, 42.7, 41.2, 26.8, 21.7; HRMS $[M + H]^+$ calcd for $C_{32}H_{30}N_3O_2$ 488.2338, found 488.2337.

The Synthesis and Characterization of Rh(III) Complex I. Indoline (**1a**, 0.1182 g, 0.6 mmol), $[Cp^*RhCl_2]_2$ (155 mg, 0.25 mmol), and NaOAc (0.1968 g, 2.40 mmol, 4 equiv) were charged into a pressure tube, to which CH_2Cl_2 (6 mL) was added. The mixture was stirred at room temperature for 48 h. The mixture was filtered through a pad of Celite. All the volatiles were removed under reduced pressure, and the solid residue was washed with diethyl ether to give a crude product, which was recrystallized in CH_2Cl_2/Et_2O to give analytically pure complex **I**. Dark red solid (0.1753 g, 75% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 4.8 Hz, 2H), 8.37 (s, 1H), 7.46−7.19 (m, 1H), 6.93 (t, J = 4.9 Hz, 1H), 6.79 (d, J = 6.5 Hz, 1H), 6.67 (t, J = 4.4 Hz, 1H), 4.35−4.20 (m, 1H), 4.11−3.92 (m, 1H), 3.29−3.12 (m, 2H), 1.42 (s, 15H). Spectral data matched those previously reported.[4d]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00650.

General experimental procedures, characterization details, and ^1H and ^{13}C NMR spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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