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Advanced Synthesis & Catalysis

Rh(III)-Catalyzed Csp^2–Csp^3 Bond Cleavage/Carbonylethylation of α-Indolyl Alcohols

Zhipeng Liu,[a] Xinwei Hu,[a] Can Yang,[a] Haisheng Xie,[a] Huanfeng Jiang,[a] and Wei Zeng[a,*]

[a] Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China
Fax: (+86)-20-2223-6337
E-mail: zengwei@scut.edu.cn

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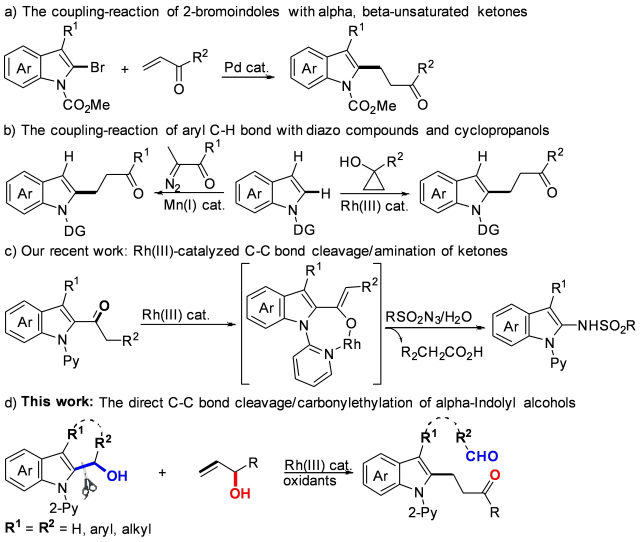
Abstract: A Rh(III)-catalyzed Csp^2–Csp^3 bond cleavage/carbonylethylation of α-indolyl alcohols with allylic alcohols has been reported. This transformation involved a cascade C–C bond cleavage/C–C bond formation, and provides a novel approach to assemble 2-carbonylethylindole skeletons.

Keywords: Rh(III)-Catalysis; Carbonylethylation; α-Indolyl alcohols; Allylic alcohols; C–C bond cleavage

Introduction

Indoles are often encountered in many natural products and bioactive small molecules.[1] Therefore, various methods have been developed in incorporating particular functional group into indole rings.[2] Among them, 2-carbonylethylindoles belong to versatile synthetic building blocks, which could be further converted into indole-fused polycyclic systems.[3] However, the synthetic access to 2-carbonylethylindoles has been rarely reported, the existed protocols mainly focus on the direct Csp^2–H and Csp^2–Br bond carbonylethylation. For examples, traditional transition metal-catalyzed cross-coupling of 2-bromoindoles with α,β-unsaturated ketones could efficiently install carbonylethyl group into 2-position of highly congested and substituted indoles (Scheme 1a).[3b,4] As for simple-structure indoles, ligand-directed coupling reaction of indolyl Csp^2–H with cyclopropanols[5] or diazo compounds[6] may regioselectively realize indolyl C2-carbonylethylation (Scheme 1b). Driven by the indole-based skeleton diversity, the development of new indolyl C2-carbonylethylation is therefore desirable.

Recently, ligand-directed unstrained carbon-carbon σ bond activation provides a straightforward approach to reorganizing complex carbon skeletons.[7] To date, this carbon-carbon cleavage strategy has been successively explored by Shi, Ackermann, Douglas, Kakiuchi, and Dong, *et al.*, to regioselectively switch



Scheme 1. Carbonylethylation strategies of indoles.

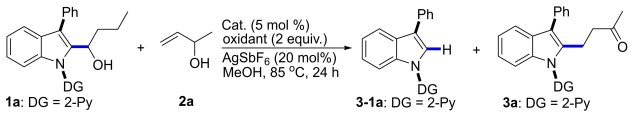
hydroxymethenyl,[8] acyl,[9] aryl,[10] allyl[11], and alkyl[12] group into alkenyl, aryl, alkyl, alkenyl, and aryl group, respectively. More recently, we reported a direct amination of ketones *via* pyridine-directed Csp^2–Csp^2 single bond activation, in which β-aryl elimination derived from enol-based cyclometallation process played a key role in this carbon-carbon bond cleavage/amination (Scheme 1c).[13] This work implied that

hydroxyl group of α-indolyl alcohols could play a similar role of enol to activate Csp^2–Csp^3 bond to enable carbon-carbon bond cleavage/functionalization. If so, once allylic alcohols are used as coupling partners to react with α-indolyl alcohols, a novel carbon-carbon σ bond cleavage/carbonylethylation could be possibly achieved (Scheme 1d).

Results and Discussion

To explore the feasibility of this transformation, the direct carbon-carbon bond cleavage/carbonylethylation of *N*-(2-pyridyl) indolylalkyl alcohol **1a** with but-3-en-2-ol **2a** was carried out by employing CH_3OH as solvent to screen different catalysts in the presence of MnO_2 (2.0 equiv.)/$AgSbF_6$ (20 mol%) under air atmosphere at 85 °C. As shown by the representative results listed in entries 1–5 of Table 1, extensive catalyst screening indicated that $[Cp^*IrCl_2]_2$ and $Cp^*Co(CO)I_2$ catalysts did not enable this transformation at all (entries 1–2). $Mn(CO)_5Br$ and $[Rh(COD)Cl]_2$ catalysts only cleavaged the indolyl Csp^2–Csp^3 bond of α-indolyl alcohol **1a**, producing 2-unsubstituted indole **3–1a** in 54% and 48% yields, respectively, and no desired 2-carbonylethylindole **3a** was observed (entries 3–4). By contrast, Rh(III)-catalyst $[Cp^*RhCl_2]_2$ simultaneously afforded 2-unsubstituted indole **3–1a** (18% yield) and 2-carbonylethylindole **3a** (42% yield) (entry 5). This result encouraged us to evaluate various oxidants by employing $[Cp^*RhCl_2]_2$ as catalysts for further increasing the chemical selectivity (entries 6–11). Gratifyingly, it was found that the use of Ag_2CO_3 led to the high-selective formation of C2-carbonylethylindole **3a** with 78% yield (entries 7–10 vs 11). Changing solvent system and reaction temperature did not produce any positive results (entries 12–16 vs 11). Meanwhile, lowering the Rh(III) catalyst-loading to 2.5 mol% could not improve the reaction conversion (entry 11 vs 17) [see the Supporting Information (SI) for screening conditions].

Table 1. Optimization of the reaction parameters.[a]



Entry	Catalysts	Oxidant	**3–1a**/**3a**[b]
1	$[Cp^*IrCl_2]_2$	MnO_2	0/0
2	$Cp^*Co(CO)I_2$	MnO_2	0/0
3	$Mn(CO)_5Br$	MnO_2	54/0
4	$[Rh(COD)Cl]_2$	MnO_2	48/0
5	$[Cp^*RhCl_2]_2$	MnO_2	18/42
6	$[Cp^*RhCl_2]_2$	AgOAc	36/0
7	$[Cp^*RhCl_2]_2$	O_2	0/0
8	$[Cp^*RhCl_2]_2$	$AgClO_4$	0/0
9	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	0/34
10	$[Cp^*RhCl_2]_2$	$AgOCOCF_3$	51/36
11	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/78
12	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/50[c]
13	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/41[d]
14	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/0[e]
15	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/47[f]
16	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/67[g]
17	$[Cp^*RhCl_2]_2$	Ag_2CO_3	0/44 [h]

[a] Unless otherwise noted, all the reactions were performed using α-indolyl alcohol **1a** (0.20 mmol), but-3-en-2-ol **2a** (0.60 mmol), $AgSbF_6$ (20 mol%), and oxidant (0.4 mmol) with catalysts (5 mol%) in MeOH (1.5 mL) at 85 °C for 24 h under air in a sealed tube, followed by flash chromatography on SiO_2.
[b] Isolated yield.
[c] Using DCE as solvent.
[d] Using THF as solvent.
[e] Using DMF as solvent.
[f] The temperature was lowered to 50 °C
[g] The temperature was increased to 100 °C
[h] The $[Cp^*RhCl_2]_2$-loading was lowered to 2.5 mol%.

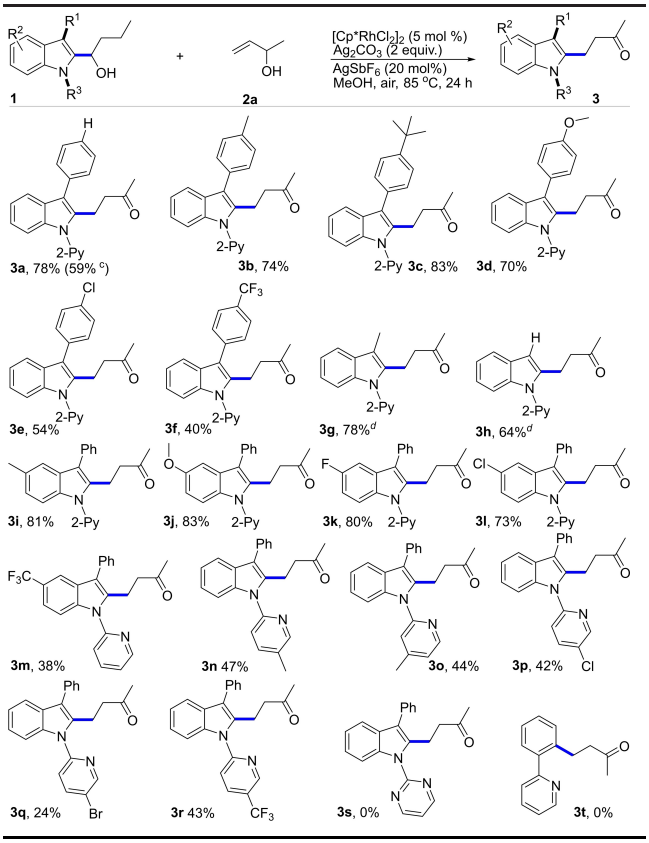
The substrate scope is presented in Table 2. As in the case of 3-phenylindoles, electron-donating (4-Me, 4-*t*Bu, 4-MeO) and electron-withdrawing (4-Cl, 4-CF_3) groups on the benzene ring of indolyl skeleton have important effects on the C–C σ bond cleavage/carbonylethylation. Among them, electron-rich phenyl substituents produced 70–83% yields of the products (**3a**~**3d**), electron-deficient phenyl substituents made the transformation a little sluggish and gave 40–54% yields of **3e** and **3f**. Meanwhile, 3-methylindole and 3-unsubstituted indole were also well-tolerated in this reaction system, affording good yields of 3-carbonylethylindoles **3g** (78%) and **3h** (64%), respectively. Similarly, this transformation is also apparently sensitive to the electronic effect of substituents at C5-position of indoles, 5-alkyl, 5-alkoxyl, and 5-halo-substituted indolyl alcohols could be efficiently converted to 2-carbonylethylindoles (**3i**~**3l**) in 73–83% yields. On the contrary, 5-trifluoromethylindolyl alcohol only furnished 38% yield of **3m**. Regretfully, the *N*-substituted pyridine-containing α-indolyl alcohols gave inferior conversions (24–47% yields for **3n**~**3r**) possibly due to the combined effects of electron and steric hindrance. It should be noted that *N*-pyrimidine-substituted α-indolylalcohol and *ortho*-pyridyl-substituted α-phenylalcohol were not allowed for this reaction system, and all the starting materials were almost completely recovered (**3s** and **3t**).

Subsequently, the effect of alkyl chain length from alkyl alcohols on this reaction was also evaluated (Table 3). It was found that reactivity of α-indolyl methanol (38% yield of **3a** from **1u**) was lower than ethyl alcohol (63% yield of **3a** from **1v**), propyl alcohol (70% yield of **3a** from **1w**) and benzyl alcohol (68% yield of **3a** from **1w**).

More importantly, indole-fused cycloalcohols **4** such as 12-, 7-, and 6-membered cycloalcohols also smoothly underwent Csp^2–Csp^3 bond cleavage/carbonylethylation to furnish the corresponding 2-carbonylethylindoles **5a**, **5b**, and **5c** in acceptable yields (42%–58%), in which the alcohol moieties were converted into aldehydes or esters (Table 4).

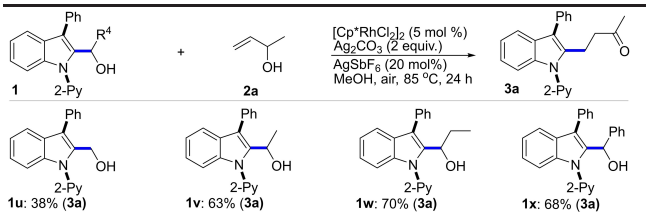
Finally, the allylic alcohols **2** were explored (Table 5). α-linear alkyl (R^6)-substituted allylic alcohols (71% yield of **6a**, 75% yield of **6c**), α-cyclohexyl (R^6)-substituted allylic alcohol (86% yield of **6b**), α-benzyl (R^6)-substituted allylic alcohols (79% yield of **6d**, 69% yield of **6f**), and even phenylethyl (R^6)-substituted allylic alcohol (87% yield of **6e**) could efficiently react with *N*-(2-pyridyl) indolylalkyl alcohol **1a** to furnish different 2-carbonylethylindoles with good to excellent yields. Notably, when homoallylic alcohol was subjected to the catalytic reaction system, 2-(3-hydroxylbutenyl)indole **6h** could be obtained in 38% yield. Unfortunately, employing internal allylic

Table 2. Substrate Scope.[a,b]



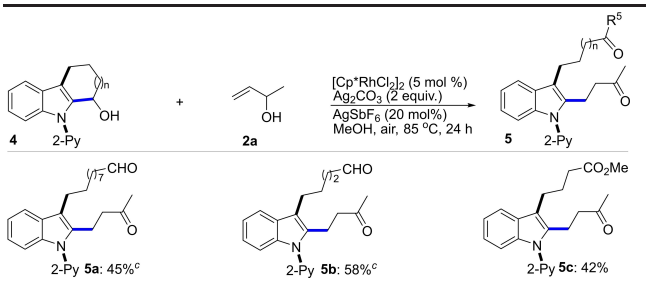
[a] All the reactions were performed using α-indolyl alcohols **1** (0.20 mmol), allylic alcohol **2a** (0.60 mmol), $AgSbF_6$ (20 mol%), and Ag_2CO_3 (0.4 mmol) with $[Cp^*RhCl_2]_2$ (5 mol%) in MeOH (1.5 mL) at 85 °C for 24 h under air in a sealed tube, followed by flash chromatography on SiO_2.
[b] Isolated yield.
[c] Large-scale reaction of **1a** (0.8 mmol).
[d] Using H_2O as solvent and without Ag_2CO_3.

Table 3. Substrate Scope.[a,b]



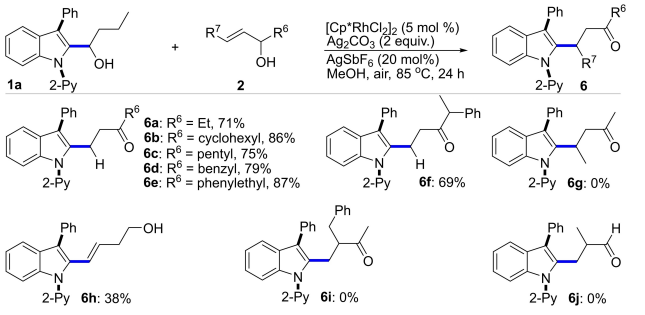
[a] All the reactions were performed using α-indolyl alcohols **1** (0.20 mmol), allylic alcohol **2a** (0.60 mmol), $AgSbF_6$ (20 mol%), and Ag_2CO_3 (0.4 mmol) with $[Cp^*RhCl_2]_2$ (5 mol%) in MeOH (1.5 mL) at 85 °C for 24 h under air in a sealed tube, followed by flash chromatography on SiO_2.
[b] Isolated yield.

Table 4. Cycloalcohol Scope.[a,b]

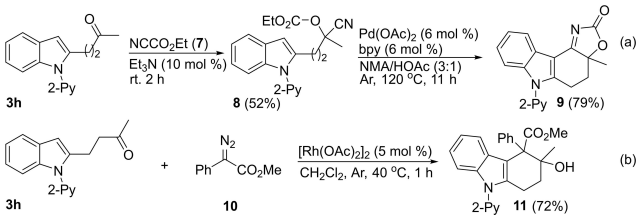


[a] All the reactions were performed using indole-fused cycloalcohols **4** (0.20 mmol), allylic alcohol **2a** (0.60 mmol), $AgSbF_6$ (20 mol%), and Ag_2CO_3 (0.4 mmol) with $[Cp^*RhCl_2]_2$ (5 mol%) in MeOH (1.5 mL) at 85 °C for 24 h under air in a sealed tube, followed by flash chromatography on SiO_2.
[b] Isolated yield.
[c] Using H_2O as solvent and without Ag_2CO_3.

Table 5. Allylic Alcohol Scope.[a,b]



[a] All the reactions were performed using α-indolyl alcohol **1a** (0.20 mmol), allylic alcohols **2** (0.60 mmol), $AgSbF_6$ (20 mol%), and Ag_2CO_3 (0.4 mmol) with $[Cp^*RhCl_2]_2$ (5 mol%) in MeOH (1.5 mL) at 85 °C for 24 h under air in a sealed tube, followed by flash chromatography on SiO_2.
[b] Isolated yield.



Scheme 2. Synthetic applications.

alcohol, 1,1-disubstituted allylic alcohols as substrates could not give the corresponding products **6 g**, **6 i** and **6 j**.

In addition, 2-carbonylethylindole **3 h** could react with ethyl carbonocyanidate **7** *via* nuclephilic reaction to afford indole-tethered nitrile **8** (52%), followed by an intramolecular cyclization in the presence of Pd(OAc)$_2$ catalysts to rapidly assemble 4,5-dihydro-3aH-oxazolo[5,4-c]carbazol-2(6H)-one **9** in 79% yield (Scheme 2a).[14] Meanwhile, the Rh(II)-catalyzed coupling-cyclization of **3 h** with diazo compound **10** could still produce 2,3,4,9-tetrahydro-1H-carbazole derivative **11** in 72% yield (Scheme 2b).[15]

To gain insight into this transformation, α-indolyl-α-phenylalcohol **1 x** was first subjected to react with but-3-en-2-ol **2 a** for 24 h, benzoic acid **12** which was possibly derived from the oxidation of benzaldehyde, could be detected and characterized by GC-MS spectrum (Scheme 3a). Then, using *N*-phenyl-indole **13** as a substrate did not lead to the formation of 2-carbonylethylindole **14** (Scheme 3b). Meanwhile, the reaction α-indolyl-α-phenylalcohol **1 x** with D_2O in the absence of allylic alcohol **2 a** under our standard condition only produced 2-unsubstituted indole *d*1-**3**–**1 a**, in which the incorporation of deuterium into C2-position at the indole ring (14% D) was observed, and no H/D exchange (0% D) of α-C–H of the alcohol *d*1-**1 x** was detected (Scheme 3c). These results indicated that pyridine played a key chelation-assisted role in the cleavage of Csp^2–Csp^3 σ bond, and a hydroxyl group-based C–C bond cleavage of α-indolyl alcohol possibly triggered this reaction. Finally, the Rh(III)-catalyzed coupling reaction of 2-unsubstituted indole **3**–**1 a** with **2 a** under the same reaction system gave 53% yield of 2-carbonylethylindole **3 a**, implying that 2-unsubstituted indole **3**–**1 a** was the possible intermediates of Csp^2–Csp^3 σ bond cleavage/functionalization (Scheme 3d).

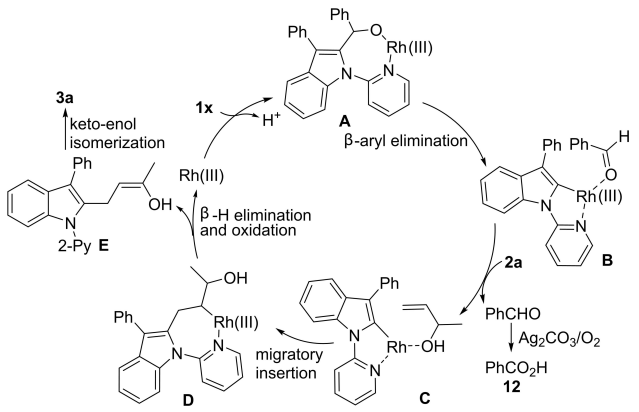
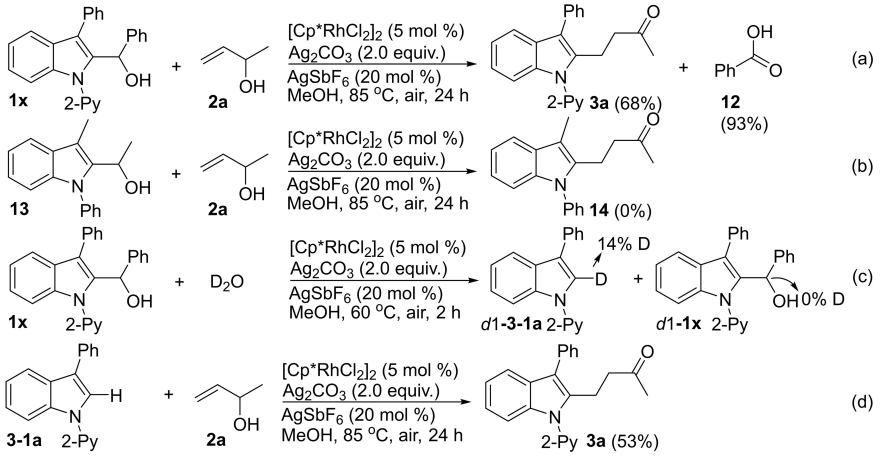


Figure 1. Possible mechanism for the transformation.

On the basis of the previous reports[13,16] and control experiments, a plausible reaction mechanism has been proposed in Figure 1. The reaction starts with the coordination of Rh(III) catalyst with pyridine "nitrogen" and alcoholic hydroxyl group to produce the cyclometallated rhodium(III) complexes **A**. Then, the C–C cleavage *via* β-aryl elimination[17] from **A** produces the corresponding Rh-aledehyde complex **B**, in which benzaldehyde could be further oxidized by Ag_2CO_3/O_2 system to benzoic acid **12** (Scheme 3a).



Scheme 3. Control experiments.

Subsequently, coordination of allylic alcohol **2a** to the rhodium center *via* ligand exchange is followed by migratory insertion to form a Rh(III)-complex **D**. Finally, the rhodium complex **D** undergoes a β-H elimination and keto-enol isomerization to give the desired 2-carbonylethylindole **3a** with the release of the Rh(I) species, which could be further oxidized to Rh(III) catalysts by Ag_2CO_3.

Conclusion

In summary, we have disclosed a novel Rh(III)-catalyzed Csp^2–Csp^3 bond cleavage/functionalization of α-indoyl alcohols *via* carbon-carbon cleavage, affording diversified 2-carbonylethylindoles. This protocol exhibited excellent functional group tolerance which rendered this reaction synthetic values for rapid assembly of highly congested and complex indoles skeletons.

Experimental Section

General Information

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Reagents were purchased from Accela, Acros, Aladdin, Adamas, Energy Chemical or TCI. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (400–630 mesh). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compounds. ^1H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature on a Bruker Avance III 400 MHz or 500 MHz for ^1H NMR and 100 MHz or 126 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass) and Thermo Scientific Q Exactive. 1-Cyclohexylprop-2-en-1-ol **2c**,[18] 1-phenylbut-3-en-2-ol **2e**,[18] 5-phenylpent-1-en-3-ol **2f**,[19] 4-phenylpent-1-en-3-ol **2g**,[19] (*E*)-pent-3-en-2-ol **2h**[20] and phenyl(2-(pyridin-2-yl)phenyl)methanol **1t**[21] were prepared according to the previous literatures.

Procedure for the Synthesis of Secondary Alcohol Substrates 1a~1r, 1v~1x, and 13

The secondary alcohols **1a~1r**, **1v~1x** and **13** were prepared from ketones **S1**, which were synthesized according to the previous literature.[13] Ketones **S1** (3.0 mmol) were dissolved in THF (20 mL), then $NaBH_4$ (15.0 mol) was added in portions, and stirred for 24~48 h at room temperature. The reaction was monitored by TLC to achieve full conversion, then quenched by saturated NH_4Cl (aq), extracted by EtOAc for three times (3× 5 mL), dried over Na_2SO_4, and evaporated in vacuum to afford the crude products, which were further purified by flash chromatography on silica gel with petroleum ether/EtOAc (20:1~5:1) to give excellent yields of the corresponding alcohols **1** and **13**.

1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1a):[22] 975 mg, 95%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J=3.6 Hz, 1H), 8.04 (t, J=7.4 Hz, 1H), 7.76 (d, J=8.0 Hz, 1H), 7.66 (dd, J=14.7, 7.5 Hz, 3H), 7.53 (t, J=7.6 Hz, 3H), 7.40 (dd, J=13.3, 6.9 Hz, 2H), 7.26 (dd, J=14.8, 7.2 Hz, 2H), 6.41 (d, J=10.4 Hz, 1H), 5.02–4.90 (m, 1H), 1.51–1.39 (m, 1H), 1.25–1.13 (m, 2H), 1.03 (dd, J=20.2, 11.8 Hz, 1H), 0.62 (t, J=6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 148.7, 139.4, 138.4, 136.2, 134.2, 130.5, 128.6, 126.9, 123.5, 122.0, 121.6, 120.4, 120.2, 120.1, 119.0, 110.0, 66.7, 37.9, 19.4, 13.7.

1-(1-(Pyridin-2-yl)-3-(*p*–tolyl)-1H-indol-2-yl)butan-1-ol (1b): white solid; 833 mg, 78% yield; m.p. 80.4–81.7 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 (dd, J=4.9, 1.2 Hz, 1H), 8.03 (m, 1H), 7.75 (d, J=8.1 Hz, 1H), 7.68 (d, J=7.7 Hz, 1H), 7.54 (d, J=8.0 Hz, 3H), 7.40–7.37 (m, 1H), 7.34 (d, J=7.8 Hz, 2H), 7.28 (dd, J=5.4, 4.2 Hz, 1H), 7.23 (dd, J=11.0, 3.9 Hz, 1H), 6.37 (d, J=10.5 Hz, 1H), 4.97 (dd, J=7.7, 2.7 Hz, 1H), 2.47 (s, 3H), 1.48–1.41 (m, 1H), 1.23–1.15 (m, 2H), 1.07–0.99 (m, 1H), 0.62 (t, J=7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 148.7, 139.4, 138.3, 136.6, 136.2, 131.2, 130.3, 129.3, 128.7, 123.5, 122.0, 121.6, 120.5, 120.2, 120.1, 110.0, 66.7, 37.9, 21.4, 19.5, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{25}N_2O$: 357.1961, found: 357.1990; IR (KBr): 3290, 3026, 2953, 2863, 1589, 1475, 1435, 1361, 1219, 1014, 825, 741, 647 cm^{-1}.

1-(3-(4-(*tert*-Butyl)phenyl)-1-(pyridin-2-yl)-1H-indol-2-yl) butan-1-ol (1c): white solid; 1051 mg, 88% yield; m.p. 159.9–162.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J=3.5 Hz, 1H), 8.03 (t, J=7.2 Hz, 1H), 7.74 (dd, J=16.7, 7.8 Hz, 2H), 7.55 (t, J=6.4 Hz, 5H), 7.42–7.35 (m, 1H), 7.26 (m, 2H), 6.40 (d, J=10.3 Hz, 1H), 4.99 (d, J=9.0 Hz, 1H), 1.44 (s, 10H), 1.20 (s, 2H), 1.04 (dd, J=16.5, 8.2 Hz, 1H), 0.63 (t, J=6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 149.7, 148.7, 139.4, 138.4, 136.3, 131.2, 130.1, 128.7, 125.5, 123.5, 122.0, 121.5, 120.6, 120.2, 120.1, 110.0, 66.7, 38.0, 34.7, 31.5, 19.5, 13.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{27}H_{31}N_2O$: 399.2431, found: 399.2503; IR (KBr): 3316, 3057, 2956, 2867, 1588, 1474, 1458, 1424, 1370, 1319, 1045, 1023, 779, 744 cm^{-1}.

1-(3-(4-Methoxyphenyl)-1-(pyridin-2-yl)-1H-indol-2-yl) butan-1-ol (1d): colorless solid; 1071 mg, 96% yield; m.p. 143.1–144.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, J=4.9, 1.2 Hz, 1H), 8.02 (m, 1H), 7.75 (d, J=8.1 Hz, 1H), 7.67 (d, J=7.3 Hz, 1H), 7.56 (dd, J=13.7, 8.4 Hz, 3H), 7.38 (dd, J=7.0, 5.3 Hz, 1H), 7.31–7.20 (m, 2H), 7.09 (d, J=8.7 Hz, 2H), 6.39 (d, J=10.4 Hz, 1H), 4.96 (dd, J=17.6, 7.5 Hz, 1H), 3.92 (s, 3H), 1.47 (m, 1H), 1.24–1.15 (m, 2H), 1.04 (m, 1H), 0.63 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 152.2, 148.7, 139.4, 138.2, 136.2, 131.5, 128.8, 126.5, 123.5, 121.9, 121.5, 120.4, 120.2, 119.8, 114.1, 110.0, 66.7, 55.3, 37.9, 19.5, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{25}N_2O_2$: 373.1911, found: 373.1968; IR (KBr): 3320, 3049, 2950, 2862,

1588, 1556, 1506, 1473, 1373, 1282, 1245, 1172, 1104, 1019, 998, 837, 791, 740 cm^{-1}.

1-(3-(4-Chlorophenyl)-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1e): light yellow solid; 812 mg, 72% yield; m.p. 171.9–173.0 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (dd, J = 4.9, 1.2 Hz, 1H), 8.04 (m, 1H), 7.76 (dd, J = 8.0, 4.5 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.54 (m, 5H), 7.42–7.39 (m, 1H), 7.31–7.27 (m, 1H), 7.24 (dd, J = 10.9, 3.9 Hz, 1H), 6.31 (d, J = 10.3 Hz, 1H), 4.90 (dd, J = 17.6, 7.5 Hz, 1H), 1.46 (m, 1H), 1.22–1.12 (m, 2H), 1.07–0.98 (m, 1H), 0.62 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 148.8, 139.5, 138.5, 136.2, 132.8, 131.7, 130.5, 128.8, 128.2, 123.7, 122.2, 121.8, 120.2, 120.1, 118.8, 110.1, 66.6, 37.8, 19.4, 13.7. HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{22}N_2OCl$: 377.1415, found: 377.1409; IR (KBr): 3310, 3061, 2954, 2861,1587, 1566, 1472, 1455, 1435, 1365, 1314, 1215, 1088, 1014, 1000, 832, 779, 746, 716 cm^{-1}.

1-(1-(Pyridin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)butan-1-ol (1f): colorless solid; 984 mg, 80% yield; m.p. 110.5–111.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.9, 1.3 Hz, 1H), 8.06 (m, 1H), 7.86–7.74 (m, 5H), 7.68 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.42 (dd, J = 7.3, 5.0 Hz, 1H), 7.36–7.25 (m, 2H), 6.38 (d, J = 10.5 Hz, 1H), 4.95 (m, 1H), 1.53–1.44 (m, 1H), 1.22–1.18 (m, 1H), 1.05 (m, 1H), 0.95–0.89 (m, 1H), 0.65 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 148.8, 139.6, 139.0, 138.3, 136.3, 130.7, 129.0(q, J = 32.3 Hz, $^2J_{CF}$), 128.0, 125.5(q, J = 4.0 Hz, $^3J_{CF}$), 124.5(d, J = 273.7 Hz, $^1J_{CF}$), 123.9, 122.4, 122.0, 120.3, 120.0, 118.7, 110.2, 66.7, 37.8, 19.5, 13.7; HR-MS (ESI) calcd for $[M-H]^-$: $C_{24}H_{20}F_3N_2O$: 409.1533, found: 409.1532; IR (KBr): 3456, 3057, 2926, 2860, 1618, 1589, 1474, 1458, 1438, 1371, 1323, 1123, 1068, 1021, 843, 782, 741 cm^{-1}.

1-(3-Methyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1g): colorless oily liquid; 756 mg, 90% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (m, 1H), 8.00–7.94 (m, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.64–7.61 (m, 1H), 7.50–7.45 (m, 1H), 7.33 (m, 1H), 7.27–7.20 (m, 2H), 6.54 (d, J = 10.1 Hz, 1H), 5.06–4.97 (m, 1H), 2.44 (s, 3H), 1.64–1.56 (m, 1H), 1.32–1.27 (m, 2H), 1.17–1.08 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 148.4, 139.3, 138.0, 136.1, 129.8, 123.1, 121.6, 120.9, 120.0, 119.5, 112.6, 109.9, 66.1, 38.2, 19.6, 13.8, 9.2; HR-MS (ESI) calcd for $[M-H]^-$: $C_{18}H_{19}N_2O$: 279.1503, found: 279.1503; IR (KBr): 3690, 3062, 2956, 2868, 1867, 1747, 1730, 1515, 1361, 1222, 780, 741 cm^{-1}.

1-(1-(Pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1h): white solid; 758 mg, 95% yield; m.p. 60.7–63.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 4.8 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.71–7.65 (m, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.38–7.33 (m, 1H), 7.26–7.20 (m, 2H), 6.71 (s, 1H), 6.11 (d, J = 2.1 Hz, 1H), 4.63 (s, 1H), 2.09–2.01 (m, 1H), 1.90 (m, 1H), 1.60 (dd, J = 14.5, 7.1 Hz, 1H), 1.45 (dd, J = 15.8, 7.2 Hz, 1H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 148.7, 143.9, 139.1, 136.6, 128.8, 122.8, 121.7, 121.3, 121.3, 120.1, 110.3, 102.8, 65.7, 36.4, 19.7, 14.1; HR-MS (ESI) calcd for $[M-H]^-$: $C_{17}H_{17}N_2O$: 265.1346, found: 265.1345; IR (KBr): 3317, 3059, 2955, 2922, 2867, 1591, 1474, 1454, 1345, 1154, 1031, 1021, 803, 746, 523 cm^{-1}.

1-(5-Methyl-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1i): colorless oily liquid; 940 mg, 88% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.65–8.57 (m, 1H), 8.02 (m, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.63 (dd, J = 8.0, 1.1 Hz, 2H), 7.53 (t, J = 7.7 Hz, 2H), 7.46–7.35 (m, 4H), 7.11 (dd, J = 8.5, 1.2 Hz, 1H), 6.43 (d, J = 10.5 Hz, 1H), 4.94 (m, 1H), 2.46 (s, 3H), 1.49–1.41 (m, 1H), 1.22–1.10 (m, 2H), 1.06–0.96 (m, 1H), 0.61 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 148.6, 139.4, 138.5, 134.5, 134.4, 131.1, 130.5, 128.8, 128.6, 126.9, 125.0, 121.8, 120.1, 120.0, 119.9, 109.8, 66.7, 37.9, 21.4, 19.4, 13.7; HR-MS (ESI) calcd for $[M-H]^-$: $C_{24}H_{23}N_2O$: 355.1816, found: 355.1816; IR (KBr): 3565, 3064, 2959, 1867, 1747, 1681, 1516, 1506, 1372, 1261, 1100, 799, 744 cm^{-1}.

1-(5-Methoxy-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl) butan-1-ol (1j): colorless oily liquid; 770 mg, 69% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, J = 5.0, 1.2 Hz, 1H), 8.02 (m, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.65–7.60 (m, 2H), 7.53 (t, J = 7.7 Hz, 2H), 7.45–7.39 (m, 2H), 7.37 (m, 1H), 7.10 (d, J = 2.5 Hz, 1H), 6.92 (dd, J = 9.0, 2.5 Hz, 1H), 6.45 (s, 1H), 4.92 (t, J = 7.5 Hz, 1H), 3.84 (s, 3H), 1.48–1.39 (m, 1H), 1.22–1.13 (m, 2H), 1.07–0.98 (m, 1H), 0.61 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 155.5, 152.2, 148.6, 139.4, 139.0, 134.4, 131.2, 130.4, 129.2, 128.6, 126.9, 121.8, 120.0, 119.9, 113.3, 110.9, 102.0, 66.7, 55.9, 37.9, 19.4, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{25}N_2O_2$: 373.1911, found: 373.1902; IR (KBr): 3260, 3036, 3011, 2988, 2953, 2863, 1473, 1441, 1206, 1150, 1069, 965, 703, 521 cm^{-1}.

1-(5-Fluoro-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1k): colorless solid; 972 mg, 90% yield; m.p. 94.3–95.9 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, J = 4.9, 1.1 Hz, 1H), 8.01 (m, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.7 Hz, 2H), 7.39 (m, 3H), 7.28 (dd, J = 9.3, 2.5 Hz, 1H), 6.97 (m, 1H), 6.28 (d, J = 10.5 Hz, 1H), 4.91 (m, 1H), 1.43–1.36 (m, 1H), 1.20–1.10 (m, 2H), 0.99 (m, 1H), 0.59 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (d, J = 238.1 Hz, $^1J_{CF}$), 152.0, 148.8, 140.0, 139.6, 133.8, 132.7, 130.3, 129.2 (d, J = 10.1 Hz, $^3J_{CF}$), 128.7, 127.1, 122.3, 120.1, 119.9, 111.6 (d, J = 26.5 Hz, $^2J_{CF}$), 110.9 (d, J = 8.8 Hz, $^3J_{CF}$), 105.4 (d, J = 23.9 Hz, $^2J_{CF}$), 66.6, 37.7, 19.4, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{22}N_2OF$: 361.1711, found: 361.1761; IR (KBr): 3379, 3305, 3082, 2961, 2927, 2866, 1588, 1472, 1444, 1370, 1137, 1024, 811, 774, 700 cm^{-1}.

1-(5-Chloro-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1l): white solid; 959 mg, 85% yield; m.p. 102.4–104.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 1H), 8.05 (t, J = 7.7 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.63–7.58 (m, 3H), 7.54 (t, J = 7.5 Hz, 2H), 7.45–7.40 (m, 3H), 7.22 (d, J = 8.8 Hz, 1H), 6.29 (d, J = 10.5 Hz, 1H), 4.94 (dd, J = 17.8, 7.6 Hz, 1H), 1.46–1.39 (m, 1H), 1.18 (m, 2H), 1.02 (dd, J = 16.8, 7.7 Hz, 1H), 0.62 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 148.8, 139.7, 139.6, 134.6, 133.6, 130.3, 129.7, 128.7, 127.2, 123.7, 122.4, 120.1, 119.8, 119.5, 111.2, 66.6, 37.7, 19.4, 13.7; HR-MS (ESI) calcd for $[M-H]^-$: $C_{23}H_{20}ClN_2O$: 375.1270, found: 375.1269; IR (KBr): 3352, 3053, 2955, 2862, 1866, 1747, 1472, 1442, 1368, 1262, 1042, 1016, 799, 704 cm^{-1}.

1-(3-Phenyl-1-(pyridin-2-yl)-5-(trifluoromethyl)-1H-indol-2-yl)butan-1-ol (1m): colorless oily liquid; 1033 mg, 84% yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.67 (m, 1H), 8.09 (m, 1H), 7.93 (s, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.63–7.60 (m, 2H), 7.59–7.53 (m, 3H), 7.51 (dd, J = 8.7, 1.4 Hz, 1H), 7.48–7.43 (m, 2H), 6.16 (d, J = 10.4 Hz, 1H), 4.96 (m, 1H), 1.44 (m, 1H), 1.21–1.13 (m,

2H), 1.08–0.99 (m, 1H), 0.62 (t, J=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 149.0, 140.2, 139.7, 137.7, 133.3, 130.4, 128.8, 128.1, 127.4, 125.0(d, J=272.7 Hz, $^1J_{CF}$), 124.0 (q, J=32.3 Hz, $^2J_{CF}$), 122.8, 120.4, 120.3, 120.2 (q, J=4.0 Hz, $^3J_{CF}$), 118.0 (q, J=5.0 Hz, $^3J_{CF}$), 110.4, 66.6, 37.7, 19.4, 13.6; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{22}F_3N_2O$: 411.1679, found: 411.1673; IR (KBr): 3437, 3056, 2961, 1473, 1442, 1325, 1272, 1162, 1115, 1000, 896, 774, 617 cm^{-1}.

1-(1-(5-Methylpyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-1-ol (1 n): white solid; 854 mg, 80% yield; m.p. 96.2–97.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48–8.42 (m, 1H), 7.84 (dd, J=8.1, 2.3 Hz, 1H), 7.68–7.62 (m, 4H), 7.54–7.48 (m, 3H), 7.44–7.36 (m, 1H), 7.26 (m, 1H), 7.24–7.19 (m, 1H), 6.37 (d, J=9.0 Hz, 1H), 4.95 (d, J=7.1 Hz, 1H), 2.50 (s, 3H), 1.48–1.40 (m, 1H), 1.22–1.13 (m, 2H), 1.07–0.99 (m, 1H), 0.62 (t, J=7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 148.7, 140.0, 138.3, 136.3, 134.3, 132.0, 130.5, 128.5, 128.4, 126.8, 123.4, 121.4, 120.3, 119.7, 119.7, 110.0, 66.7, 37.9, 19.5, 18.1, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{25}N_2O$: 357.1961, found: 357.1992; IR (KBr): 3265, 3047, 2954, 2926, 1599, 1484, 1455, 1390, 1219, 1012, 961, 745, 704 cm^{-1}.

1-(1-(4-Methylpyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-1-ol (1 o): colorless solid; 929 mg, 87% yield; m.p. 84.6–86.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J=5.2 Hz, 1H), 7.69–7.62 (m, 3H), 7.57–7.50 (m, 4H), 7.43–7.39 (m, 1H), 7.27 (m, 1H), 7.24–7.20 (m, 2H), 6.53 (d, J=10.1 Hz, 1H), 4.95 (d, J=9.6 Hz, 1H), 2.58 (s, 3H), 1.44 (m, 1H), 1.25–1.14 (m, 2H), 1.09–0.99 (m, 1H), 0.63 (t, J=7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 151.2, 148.2, 138.5, 136.2, 134.3, 130.5, 128.5, 126.9, 123.4, 123.2, 121.5, 120.7, 120.4, 119.9, 110.1, 66.6, 37.9, 21.5, 19.5, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{25}N_2O$: 357.1961, found: 357.1989; IR (KBr): 3516, 2978, 2960, 2866, 1752, 1735, 1700, 1654, 1457, 1220, 1068, 746, 699 cm^{-1}.

1-(1-(5-Chloropyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-1-ol (1 p): colorless solid; 1038 mg, 92% yield; m.p. 128.7–129.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J=2.4 Hz, 1H), 8.00 (dd, J=8.6, 2.6 Hz, 1H), 7.72 (d, J=8.6 Hz, 1H), 7.68 (d, J=7.8 Hz, 1H), 7.66–7.63 (m, 2H), 7.54 (t, J=7.7 Hz, 2H), 7.49 (d, J=8.2 Hz, 1H), 7.43 (t, J=7.4 Hz, 1H), 7.33–7.29 (m, 1H), 7.27–7.23 (m, 1H), 5.78 (d, J=9.8 Hz, 1H), 4.97 (q, J=7.8 Hz, 1H), 1.53–1.46 (m, 1H), 1.22 (m, 2H), 1.09–1.02 (m, 1H), 0.65 (t, J=7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 147.6, 139.2, 138.1, 136.2, 134.0, 130.4, 129.9, 128.6, 127.1, 123.8, 121.9, 121.1, 120.6, 109.8, 66.7, 37.9, 19.5, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{22}ClN_2O$: 377.1415, found: 377.1419; IR (KBr): 3297, 3043, 2953, 2862, 1576, 1459, 1390, 1361, 1110, 1035, 776, 747 cm^{-1}.

1-(1-(5-Bromopyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-1-ol (1 q): light yellow solid; 844 mg, 67% yield; m.p. 111.2–112.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J=1.8 Hz, 1H), 8.12 (dd, J=8.4, 1.9 Hz, 1H), 7.68 (dd, J=15.0, 8.1 Hz, 4H), 7.55 (t, J=7.5 Hz, 2H), 7.50 (d, J=8.2 Hz, 1H), 7.44 (t, J=7.3 Hz, 1H), 7.33–7.24 (m, 2H), 5.82 (d, J=10.2 Hz, 1H), 5.06–4.88 (m, 1H), 1.58–1.47 (m, 1H), 1.31–1.17 (m, 2H), 1.07 (m, 1H), 0.67 (t, J=7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 149.8, 142.1, 138.1, 136.2, 134.1, 130.5, 128.7, 127.1, 123.9, 122.0, 121.4, 120.7, 120.6, 118.0, 109.9, 66.7, 37.9, 19.5, 13.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{22}BrN_2O$: 421.0910, found: 421.0915; IR (KBr): 3305, 3039, 2953, 2922, 1571, 1454, 1470, 1458, 1034, 1012, 775, 753, 703 cm^{-1}.

1-(3-Phenyl-1-(5-(trifluoromethyl)pyridin-2-yl)-1H-indol-2-yl)butan-1-ol (1 r): colorless solid; 935 mg, 76% yield; m.p. 72.8–73.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, J=0.8 Hz, 1H), 8.27 (dd, J=8.5, 2.3 Hz, 1H), 7.91 (d, J=8.5 Hz, 1H), 7.67 (d, J=7.6 Hz, 1H), 7.65–7.61 (m, 2H), 7.54 (dd, J=15.0, 7.7 Hz, 3H), 7.46–7.40 (m, 1H), 7.34–7.30 (m, 1H), 7.28–7.24 (m, 1H), 5.85 (d, J=10.3 Hz, 1H), 4.96 (m, 1H), 1.51–1.44 (m, 1H), 1.25–1.14 (m, 2H), 1.08–1.00 (m, 1H), 0.63 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 146.0 (q, J=4.0 Hz, $^3J_{CF}$), 138.2, 136.7 (q, J=4.0 Hz, $^3J_{CF}$), 136.1, 133.7, 130.4, 129.0, 128.7, 127.3, 124.2, 124.1(q, J=24.2 Hz, $^2J_{CF}$), 123.3 (d, J=272.7 Hz, $^1J_{CF}$), 122.4, 121.6, 120.8, 119.7, 109.9, 66.7, 38.0, 19.4, 13.6; HR-MS (ESI) calcd for $[M-H]^-$: $C_{24}H_{20}F_3N_2O$: 409.1533, found: 409.1533; IR (KBr): 3364, 3052, 2956, 2867, 1602, 1489, 1456, 14325, 1169, 1133, 1081, 1019, 749, 702 cm^{-1}.

1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)ethan-1-ol (1 v): light yellow solid; 829 mg, 88% yield; m.p. 148.5–150.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68–8.62 (m, 1H), 8.04 (m, 1H), 7.78 (d, J=8.1 Hz, 1H), 7.69 (d, J=7.6 Hz, 1H), 7.65 (dd, J=8.0, 1.1 Hz, 2H), 7.56–7.52 (m, 3H), 7.44–7.38 (m, 2H), 7.29 (m, 1H), 7.25–7.22 (m, 1H), 6.52 (s, 1H), 5.20 (s, 1H), 1.15 (d, J=7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 148.7, 139.4, 139.3, 136.2, 134.2, 130.5, 128.6, 128.5, 127.0, 123.6, 122.0, 121.7, 120.5, 120.3, 119.1, 110.0, 62.4, 22.2; HR-MS (ESI) calcd for $[M+H]^+$: $C_{21}H_{19}N_2O$: 315.1492, found: 315.1510; IR (KBr): 3211, 3025, 2959, 1867, 1747, 1730, 1506, 1539, 1361, 1224, 094, 1018, 771, 748 cm^{-1}.

1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)propan-1-ol (1 w): colorless liquid; 925 mg, 94% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65–8.60 (m, 1H), 8.03 (m, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.67 (dd, J=15.0, 7.4 Hz, 3H), 7.54 (t, J=7.8 Hz, 3H), 7.44–7.37 (m, 2H), 7.31–7.27 (m, 1H), 7.24 (t, J=7.4 Hz, 1H), 6.38 (d, J=10.4 Hz, 1H), 4.87 (dd, J=18.0, 7.9 Hz, 1H), 1.53–1.45 (m, 1H), 1.28–1.21 (m, 1H), 0.68 (t, J=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 148.7, 139.4, 138.2, 136.2, 134.3, 130.5, 128.6, 127.0, 123.6, 122.0, 121.6, 120.4, 120.3, 120.2, 110.0, 68.4, 28.8, 10.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{22}H_{21}N_2O$: 329.1648, found: 329.1669; IR (KBr): 3674, 3026, 2967, 2922, 2869, 1867, 1588, 1471, 1439, 1222, 1091, 1962, 741, 703 cm^{-1}.

Phenyl(3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)methanol (1 x): white power; 948 mg, 84% yield; m.p. 167.0–168.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, J=5.0, 1.2 Hz, 1H), 7.86–7.78 (m, 3H), 7.64 (m, 1H), 7.57 (t, J=7.7 Hz, 2H), 7.49 (dd, J=7.0, 1.5 Hz, 1H), 7.44 (t, J=7.4 Hz, 1H), 7.34–7.25 (m, 3H), 7.10 (m, 1H), 7.09–7.05 (m, 2H), 7.00 (dd, J=16.2, 9.3 Hz, 3H), 6.94 (t, J=7.2 Hz, 1H), 6.27 (d, J=11.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 148.1, 142.8, 138.9, 138.3, 136.2, 134.0, 130.3, 128.8, 128.1, 127.4, 127.2, 126.1, 125.2, 123.8, 121.7, 121.6, 121.2, 120.6, 120.2, 110.2, 67.4; HR-MS (ESI) calcd for $[M+H]^+$: $C_{26}H_{21}N_2O$: 377.1648, found: 377.1675; IR (KBr): 3409, 3026, 2927, 1589, 1488, 1434, 1367, 1149, 1039, 774, 756, 609 cm^{-1}.

1-(3-Methyl-1-phenyl-1H-indol-2-yl)ethan-1-ol (13): light yellow power; 685 mg, 91% yield; m.p. 122.3–124.0 °C; ^{1}H

NMR (400 MHz, CDCl3) δ 7.66 (m, 1H), 7.59–7.47 (m, 3H), 7.41 (d, J = 7.5 Hz, 2H), 7.25–7.14 (m, 2H), 7.08–7.01 (m, 1H), 5.06 (q, J = 6.8 Hz, 1H), 2.56 (s, 3H), 1.56 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3, 137.8, 129.5, 128.9, 128.8, 128.1, 122.3, 119.8, 118.6, 110.3, 109.0, 63.6, 22.9, 9.1; HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{18}NO$: 252.1383, found: 252.1374; IR (KBr): 3436, 3067, 2966, 1923, 1637, 1498, 1454, 1370, 1110, 1070, 760, 742, 700 cm^{-1}.

Procedure for the Synthesis of Primary Alcohols 1 s and 1 u

The alcohols **1 s** and **1 u** were prepared from ketones **S2**, which were synthesized according to the previous literature.[13] To a 35 mL pressure tube equipped with a stirring bar were added $[Mn(CO)_5Br]$ (2 mg, 0.005 mmol), $(CH_2O)_n$ (90.0 mg, 3.0 mmol), NaOAc (8.0 mg, 0.10 mmol) and ketones (1.0 mmol) under air. The reaction vessel was evacuated and backfilled with argon for three times. Dioxane (1.0 mL) was added under an argon atmosphere, the tube was sealed and the reaction was stirred for 15 h at 80 °C. The mixture was cooled to room temperature and concentrated afterwards. Purification by column chromatography on silica gel (eluent: pentane/ethyl acetate = 15:1) afforded the pure desired products **1 s** and **1 u**.

(3-Phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanol (1 s): light yellow power; 200 mg, 66% yield; m.p. 138.1–138.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 4.9 Hz, 2H), 8.59 (d, J = 8.4 Hz, 1H), 7.75 (dd, J = 8.1, 1.3 Hz, 3H), 7.58 (dd, J = 10.5, 4.7 Hz, 2H), 7.48–7.37 (m, 2H), 7.37–7.29 (m, 1H), 7.15 (t, J = 4.9 Hz, 1H), 5.50 (t, J = 7.3 Hz, 1H), 4.74 (d, J = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 157.8, 136.1, 135.7, 133.6, 130.2, 128.9, 128.7, 127.3, 124.7, 123.0, 122.8, 120.1, 116.8, 115.1, 55.7; HR-MS (ESI) calcd for $[M–H]^-$: $C_{19}H_{14}N_3O$: 300.1142, found: 300.1142; IR (KBr): 3262, 3042, 2929, 2883, 1565, 1453, 1430, 1268, 1231, 1010, 783, 728 cm^{-1}.

(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)methanol (1 u): white power; 210 mg, 70% yield; m.p. 104.3–105.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 4.2 Hz, 1H), 7.95–7.87 (m, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 9.0 Hz, 3H), 7.57 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.29–7.19 (m, 3H), 5.68 (t, J = 6.8 Hz, 1H), 4.58 (d, J = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 148.9, 139.2, 136.6, 135.6, 134.1, 130.0, 128.8, 128.3, 126.9, 123.8, 121.9, 121.6, 120.6, 119.7, 119.6, 110.5, 55.1; HR-MS (ESI) calcd for $[M–H]^-$: $C_{20}H_{15}N_2O$: 299.1190, found: 299.1190; IR (KBr): 3325, 3018, 2925, 2855, 1592, 1473, 1439, 1367, 1233, 1199, 1077, 1055, 924, 727, 704, 649 cm^{-1}.

Procedure for the Synthesis of Indole-Fused Cycloalcohols 4 a, 4 b and 4 c

General procedure for the synthesis of arylalkylketone **S3**: Indole (3.0 mmol) was coupled with 2-bromopyridine (569 mg, 3.6 mmol) using $K_3PO_4 \cdot 3H_2O$ (1.68 g, 6.3 mmol), CuI (29 mg, 1.5 mmol), and *N*, *N*-dimethylcyclohexane-1,2-diamine (85 mg, 6.0 mmol). Flash chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) provided of the desired product **S3**.[13,23]

5-(Pyridin-2-yl)-7,8,9,10-tetrahydrocyclohepta[b]indol-6(5H)-one (S3): white solid; 432 mg, 55% yield; m.p. 108.7–110.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.0 Hz, 1H), 7.87 (m, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.39–7.30 (m, 4H), 7.27–7.21 (m, 1H), 3.24–3.16 (m, 2H), 2.89–2.84 (m, 2H), 2.09–1.99 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 152.3, 149.2, 139.4, 138.0, 134.8, 128.3, 127.4, 126.9, 122.2, 121.6, 121.2, 121.0, 111.3, 42.9, 25.8, 24.0, 22.3; HR-MS [ESI-MS(+)] calcd for $[M+H]^+$: $C_{18}H_{17}N_2O$: 277.1335, found: 277.1332; IR (KBr): 3465, 3051, 2926, 2854, 1747, 1704, 1649, 1589, 1468, 1220, 1150, 1135, 1049, 778, 744, 684 cm^{-1}.

Compounds **4 a**, **4 b**, **4 c** was prepared from the compound **S3** according to the procedure for the synthesis of compound **1 b**.

5-(Pyridin-2-yl)-6,7,8,9,10,11,12,13,14,15-decahydro-5H-cyclododeca[b]indol-6-ol (4 a): white power; 564 mg, 54% yield; m.p. 122.2–124.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63–8.52 (m, 1H), 7.99 (m, 1H), 7.73–7.61 (m, 2H), 7.51–7.45 (m, 1H), 7.34 (dd, J = 7.3, 5.1 Hz, 1H), 7.27–7.19 (m, 2H), 6.57 (d, J = 10.7 Hz, 1H), 5.17 (m, 1H), 3.05–2.91 (m, 2H), 2.02–1.93 (m, 1H), 1.82 (m, 2H), 1.60 (m, 2H), 1.44–1.32 (m, 4H), 1.28–1.09 (m, 6H), 0.92–0.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 148.3, 140.1, 139.3, 136.7, 129.1, 123.1, 121.6, 120.9, 120.2, 120.0, 116.8, 109.9, 62.4, 32.7, 28.0, 25.9, 23.7, 23.6, 22.9, 22.0, 21.7, 20.9; HR-MS (ESI) calcd for $[M–H]^-$: $C_{23}H_{27}N_2O$: 347.2129, found: 347.2127; IR (KBr): 3289, 3050, 2925, 2850, 1588, 1567, 1474, 1437, 1212, 992, 935, 786, 743, 681 cm^{-1}.

5-(Pyridin-2-yl)-5,6,7,8,9,10-hexahydrocyclohepta[b]indol-6-ol (4 b): white power; 150 mg, 54% yield; m.p. 98.7–99.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 4.6 Hz, 1H), 7.92–7.86 (m, 1H), 7.71–7.65 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.53–7.46 (m, 1H), 7.26 (dd, J = 7.9, 4.7 Hz, 3H), 5.61 (s, 1H), 4.97–4.85 (m, 1H), 3.13–2.95 (m, 2H), 2.42–2.18 (m, 3H), 2.05 (t, J = 12.9 Hz, 1H), 1.98–1.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 148.9, 139.4, 139.0, 135.3, 129.3, 123.0, 121.5, 120.9, 120.2, 119.3, 117.9, 110.0, 65.0, 32.1, 27.6, 23.1; HR-MS [ESI-MS(+)] calcd for $[M+H]^+$: $C_{18}H_{19}N_2O$: 279.1492, found: 279.1490; IR (KBr): 3451, 2928, 1634, 1591, 1475, 1457, 1367, 1218, 1095, 1002, 775, 739 cm^{-1}.

9-(Pyridin-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-1-ol (4 c): white power; 180 mg, 68% yield; m.p.105.2–107.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 4.9, 1.1 Hz, 1H), 7.94 (m, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.65–7.58 (m, 2H), 7.31–7.22 (m, 3H), 6.25 (s, 1H), 4.76 (s, 1H), 2.96 (m, 1H), 2.73–2.62 (m, 1H), 2.31 (dd, J = 12.3, 2.3 Hz, 1H), 2.26–2.13 (m, 1H), 2.01–1.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 148.6, 139.0, 137.7, 135.5, 128.7, 123.2, 121.1, 120.7, 119.4, 118.5, 115.2, 110.4, 60.5, 31.0, 21.5, 18.0; HR-MS [ESI-MS(+)] calcd for $[M+H]^+$: $C_{17}H_{17}N_2O$: 265.1335, found: 265.1331; IR (KBr): 3296, 2946, 2920, 2852, 1590, 1474, 1444, 1371, 1308, 1227, 1168, 983, 756, 743 cm^{-1}.

Procedure for the Synthesis of Allylic Alcohol 2 j

Synthesis of 2-benzylacrylaldehyde S4: To a solution of formaldehyde (10 mmol, 37% in water) and 3-phenylpropanal (10 mmol, 100 mol%) in *i*-PrOH (1 mL/mmol) was added propionic acid (1 mmol, 10 mol%) and pyrrolidine (1 mmol, 10 mol%). The reaction mixture was stirred at 45 °C for

20 hours. $NaHCO_3$ (3 mL/mmol) was added and the mixture was extracted with CH_2Cl_2 (3×2 mL/mmol). The combined organic extracts were washed with brine (3 mL/mmol), dried (Na_2SO_4), and concentrated *in vacuo*. Purification of the residue by flash chromatography (petroleum ether: ethyl acetate = 30:1), afforded the corresponding aldehyde.[24]

2-Benzylacrylaldehyde (S4):[24] yellow oil; 1.21 g, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.36–7.18 (m, 5H), 6.12 (d, J = 15.5 Hz, 2H), 3.60 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 149.8, 138.2, 135.2, 129.2, 128.6, 126.5, 34.2.

Synthesis of 3-benzylbut-3-en-2-ol 2 j: To a solution of MeLi (6.0 mL, 1.6 M in Et_2O, 9.6 mmol) in anhydrous THF (5 mL) at 0 °C was added a solution of the 2-benzylacrylaldehyde **S4** (876 mg, 6 mmol) in anhydrous THF (5 mL) dropwise. The reaction mixture was stirred at room temperature for 1 hour before addition of saturated aqueous NH_4Cl (20 mL). The resulting phases were separated, and the aqueous phase was extracted with Et_2O (2×20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo* to afford the title compound.[25]

3-Benzylbut-3-en-2-ol (2 j):[25] yellow oil; 923 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 2H), 7.25 (t, J = 6.7 Hz, 3H), 5.18 (s, 1H), 4.78 (s, 1H), 4.28 (q, J = 6.3 Hz, 1H), 3.51 (d, J = 15.5 Hz, 1H), 3.39 (d, J = 15.5 Hz, 1H), 1.68 (s, 1H), 1.34 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 139.5, 129.2, 128.4, 126.2, 110.9, 70.2, 39.0, 22.2.

Procedure for the Synthesis of Compound 3–1 a

An oven-dried sealed tube charged **1 a** (0.20 mmol), **2 a** (0.40 mmol), $AgSbF_6$ (20 mol%), MnO_2 (0.4 mmol), $Mn(CO)_5Br$ (5 mol%), and MeOH (1.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at 85 °C for 24 h. The mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:6) as eluent to afford the desired product **3–1 a**.

3-Phenyl-1-(pyridin-2-yl)-1H-indole 3-1 a:[13] 29 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 4.8, 0.9 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.93 (s, 1H), 7.85 (m, J = 8.2, 1.8 Hz, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.60–7.51 (m, 3H), 7.40 (q, J = 6.8 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.21 (dd, J = 7.3, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 149.1, 138.5, 135.9, 134.8, 128.9, 128.6, 127.9, 126.6, 123.6, 123.5, 121.8, 120.8, 120.2, 120.2, 114.7, 113.3.

Procedure for the Synthesis of Compounds 3 a ~ 3 f, 3 i ~ 3 r, 5 c, 6 a ~ 6 f and 6 h

An oven-dried sealed tube charged **1** or **4** (0.20 mmol), **2** (0.40 mmol), $AgSbF_6$ (20 mol%), Ag_2CO_3 (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), and MeOH (1.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at 85 °C for 24 h. The mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:10 ~ 1:5) as eluent to afford the desired products.

4-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3 a): yellow oil; 53 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 3.4 Hz, 1H), 7.96 (m, 1H), 7.63 (d, J = 6.8 Hz, 1H), 7.58–7.49 (m, 5H), 7.38 (dd, J = 10.8, 6.2 Hz, 3H), 7.24–7.16 (m, 2H), 3.31–3.19 (m, 2H), 2.65–2.51 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 151.4, 149.8, 138.6, 136.7, 135.9, 134.8, 129.9, 128.7, 128.3, 126.6, 122.6, 122.4, 121.4, 121.1, 119.2, 117.7, 110.1, 43.6, 29.6, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{21}N_2O$: 341.1640, found: 341.1648; IR (KBr): 3474, 1747, 1715, 1705, 1647, 1506, 1275, 1261, 898, 749 cm^{-1}.

4-(1-(Pyridin-2-yl)-3-(p–tolyl)-1H-indol-2-yl)butan-2-one (3 b): colorless solid; 52 mg, 74% yield; m.p. 89.0–92.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 4.8, 1.3 Hz, 1H), 7.95 (dd, J = 7.7, 1.9 Hz, 1H), 7.62 (dd, J = 6.7, 1.9 Hz, 1H), 7.57–7.54 (m, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.40–7.35 (m, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.23–7.15 (m, 2H), 3.28–3.19 (m, 2H), 2.61–2.53 (m, 2H), 2.46 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 151.4, 149.8, 138.6, 136.7, 136.2, 135.7, 131.7, 129.8, 129.4, 128.4, 122.5, 122.4, 121.4, 121.0, 119.3, 117.6, 110.1, 43.6, 29.6, 21.3, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_2O$: 355.1799, found: 355.1805; IR (KBr): 3818, 3617, 2314, 1715, 1470, 1437, 1369, 742 cm^{-1}.

4-(3-(4-(*tert*-Butyl)phenyl)-1-(pyridin-2-yl)-1H-indol-2-yl) butan-2-one (3 c): yellow oil; 66 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74–8.65 (m, 1H), 7.96 (m, 1H), 7.69–7.64 (m, 1H), 7.55 (dd, J = 13.3, 8.2 Hz, 3H), 7.48 (d, J = 8.3 Hz, 2H), 7.41–7.36 (m, 2H), 7.23–7.16 (m, 2H), 3.30–3.22 (m, 2H), 2.62–2.55 (m, 2H), 1.97 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 151.5, 149.8, 149.3, 138.6, 136.7, 135.8, 131.6, 129.5, 128.4, 125.6, 122.5, 122.3, 121.3, 121.0, 119.4, 117.6, 110.0, 43.7, 34.6, 31.5, 29.6, 19.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{27}H_{29}N_2O$: 397.2268, found: 397.2274; IR (KBr): 3901, 3565, 1799, 1747, 1714, 1689, 1516, 1456, 742 cm^{-1}.

4-(3-(4-Methoxyphenyl)-1-(pyridin-2-yl)-1H-indol-2-yl) butan-2-one (3 d): brown oil; 52 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.5 Hz, 1H), 7.96 (t, J = 7.6 Hz, 1H), 7.58 (dd, J = 15.7, 7.7 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.41–7.35 (m, 2H), 7.23–7.16 (m, 2H), 7.06 (d, J = 8.2 Hz, 2H), 3.91 (s, 3H), 3.29–3.16 (m, 2H), 2.59–2.51 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 158.4, 151.4, 149.8, 138.6, 136.6, 135.6, 131.0, 128.5, 127.0, 122.5, 122.3, 121.3, 121.0, 119.2, 117.3, 114.2, 110.1, 55.3, 43.6, 29.6, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_2O_2$: 371.1754, found: 371.1750; IR (KBr): 3853, 3728, 2925, 1716, 1585, 1470, 1369, 1245, 835 cm^{-1}.

4-(3-(4-Chlorophenyl)-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3 e): colorless solid; 40 mg, 54% yield; m.p. 101.4–103.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.7 Hz, 1H), 7.97 (t, J = 7.7 Hz, 1H), 7.57 (t, J = 7.9 Hz, 2H), 7.48 (s, 4H), 7.43–7.34 (m, 2H), 7.25–7.16 (m, 2H), 3.30–3.16 (m, 2H), 2.62–2.48 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 151.2, 149.9, 138.7, 136.7, 136.1, 133.3, 132.5, 131.1, 128.9, 128.0, 122.7, 122.6, 121.4, 121.3, 118.9, 116.4, 110.2, 43.4, 29.7, 19.6; HR-MS (ESI) calcd for $[M+H]^+$:

$C_{23}H_{20}ClN_2O$: 375.1252, found: 375.1259; IR (KBr): 3595, 1716, 1586, 1469, 1437, 1369, 1235, 1089, 1012, 831, 742 cm^{-1}.

4-(1-(Pyridin-2-yl)-3-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)butan-2-one (3f): yellow oil; 33 mg, 40% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.8, 1.2 Hz, 1H), 7.99 (m, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.64–7.54 (m, 2H), 7.42 (dd, J = 7.0, 5.3 Hz, 1H), 7.39–7.33 (m, 1H), 7.23 (m, 2H), 3.29–3.16 (m, 2H), 2.63–2.47 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 151.1, 149.9, 138.8, 138.7, 136.8, 136.5, 130.0, 128.6 (q, J = 32.3 Hz, $^2J_{CF}$), 127.8, 125.7 (q, J = 4.0 Hz, $^3J_{CF}$), 124.4 (d, J = 282.8 Hz, $^1J_{CF}$), 122.9, 122.7, 121.5, 121.4, 118.9, 116.3, 110.3, 43.4, 29.6, 19.6; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{20}F_3N_2O$: 409.1522, found: 409.1520; IR (KBr): 3839, 3713, 3565, 1867, 1715, 1516, 1338, 1266, 953, 742 cm^{-1}.

4-(5-Methyl-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3i): colorless solid; 57 mg, 81% yield; m.p. 90.1–93.4 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 4.7 Hz, 1H), 7.95 (m, 1H), 7.53 (dd, J = 16.2, 8.0 Hz, 5H), 7.43–7.34 (m, 3H), 7.30–7.27 (m, 1H), 7.05 (d, J = 8.4 Hz, 1H), 3.25 (dd, J = 10.2, 5.6 Hz, 2H), 2.61–2.55 (m, 2H), 2.46 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 151.5, 149.8, 138.6, 136.0, 135.0, 134.9, 130.5, 130.0, 128.7, 128.5, 126.6, 124.0, 122.2, 121.2, 118.9, 117.4, 109.8, 43.6, 29.6, 21.5, 19.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_{2.1}O$: 355.1799, found: 355.1805; IR (KBr): 3491, 1715, 1686, 1588, 1471, 1438, 1370, 770, 745, 702 cm^{-1}.

4-(5-Methoxy-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl) butan-2-one (3j): colorless solid; 61 mg, 83% yield; m.p. 80.2–83.6 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.67 (dd, J = 4.9, 1.2 Hz, 1H), 7.94 (m, 1H), 7.57–7.48 (m, 5H), 7.38 (m, 2H), 7.29–7.27 (m, 1H), 7.07 (d, J = 2.4 Hz, 1H), 6.86 (dd, J = 8.9, 2.5 Hz, 1H), 3.83 (s, 3H), 3.22 (dd, J = 8.8, 7.0 Hz, 2H), 2.61–2.49 (m, 2H), 1.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 155.3, 151.5, 149.8, 138.6, 136.5, 134.9, 131.8, 129.8, 128.8, 126.6, 122.2, 121.1, 117.5, 112.3, 111.0, 101.1, 55.9, 43.6, 29.6, 19.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_2O_2$: 371.1749, found: 371.1754; IR (KBr): 3648, 2923, 1715, 1582, 1472, 1440, 1370, 1271, 1208, 1162, 796, 770, 703 cm^{-1}.

4-(5-Fluoro-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3k): brown oil; 57 mg, 80% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.7 Hz, 1H), 7.97 (t, J = 7.7 Hz, 1H), 7.52 (t, J = 6.3 Hz, 5H), 7.41–7.37 (m, 2H), 7.30–7.26 (m, 2H), 6.93 (dd, J = 12.5, 5.4 Hz, 1H), 3.28–3.16 (m, 2H), 2.62–2.54 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 158.9 (d, J = 236.3 Hz, $^1J_{CF}$), 151.2, 149.9, 138.8, 137.5, 134.3, 133.2, 129.7, 128.8, 128.7 (d, J = 8.1 Hz, $^3J_{CF}$), 126.8, 122.7, 121.3, 117.6, 110.9 (d, J = 10.1 Hz, $^3J_{CF}$), 110.6 (d, J = 26.3 Hz, $^2J_{CF}$), 104.3 (d, J = 24.2 Hz, $^2J_{CF}$), 43.4, 29.6, 19.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{20}FN_2O$: 359.1546, found: 359.1554; IR (KBr): 3627, 2923, 1716, 1584, 1472, 1441, 1372, 1265, 1139, 795, 742, 702 cm^{-1}.

4-(5-Chloro-3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3l): yellow oil; 55 mg, 73% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.6 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.57 (s, 1H), 7.52 (d, J = 11.7 Hz, 5H), 7.44–7.38 (m, 2H), 7.28 (d, J = 4.3 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 3.25–3.15 (m, 2H), 2.59–2.52 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 151.0, 150.0, 138.8, 137.3, 135.1, 134.1, 129.8, 129.4, 128.8, 126.9, 126.8, 122.8, 122.7, 121.4, 118.7, 117.2, 111.2, 43.3, 29.6, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{20}ClN_2O$: 375.1251, found: 375.1259; IR (KBr): 3500, 1715, 1586, 1471, 1453, 1440, 1368, 1267, 1179, 1070, 954, 796, 768, 703 cm^{-1}.

4-(3-Phenyl-1-(pyridin-2-yl)-5-(trifluoromethyl)-1H-indol-2-yl)butan-2-one (3m): yellow oil; 31 mg, 38% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 3.2 Hz, 1H), 8.00 (m, 1H), 7.87 (s, 1H), 7.53 (m, 5H), 7.46–7.38 (m, 4H), 3.26–3.18 (m, 2H), 2.60–2.51 (m, 2H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 150.8, 150.1, 138.9, 138.0, 137.8, 133.8, 129.8, 128.9, 127.8, 127.1, 124.3(d, J = 277.8 Hz, $^1J_{CF}$), 123.5 (q, J = 32.3 Hz, $^2J_{CF}$), 123.1, 121.6, 119.3 (q, J = 3.0 Hz, $^3J_{CF}$), 118.1, 116.9 (q, J = 4.0 Hz, $^3J_{CF}$), 110.4, 43.2, 29.6, 19.6; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{20}F_3N_2O$: 409.1522, found: 409.1514; IR (KBr): 3605, 2922, 2854, 1716, 1584, 1470, 1440, 1370, 1325, 1275, 1160, 1112, 1057, 767, 701 cm^{-1}.

4-(1-(5-Methylpyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-2-one (3n): colorless solid; 33 mg, 47% yield; m.p. 137.7–141.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.57–7.49 (m, 4H), 7.44 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.1 Hz, 1H), 7.33–7.28 (m, 1H), 7.23–7.15 (m, 2H), 3.25–3.16 (m, 2H), 2.62–2.55 (m, 2H), 2.48 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 150.1, 148.9, 139.2, 136.9, 135.9, 134.9, 132.3, 129.9, 128.7, 128.1, 126.5, 122.4, 121.0, 120.9, 119.1, 117.2, 110.1, 43.6, 29.7, 19.7, 18.1; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_2O$: 355.1798, found: 355.1805; IR (KBr): 3624, 2925, 1716, 1483, 1458, 1397, 1363, 1238, 1189, 836, 775, 744, 703 cm^{-1}.

4-(1-(4-Methylpyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-2-one (3o): yellow oil; 31 mg, 44% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 5.0 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.54 (m, 4H), 7.38 (dd, J = 13.7, 7.6 Hz, 3H), 7.26–7.15 (m, 3H), 3.36–3.12 (m, 2H), 2.67–2.55 (m, 2H), 2.53 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 151.4, 150.2, 149.4, 136.8, 135.9, 134.9, 129.9, 128.7, 128.2, 126.6, 123.7, 122.5, 122.1, 121.0, 119.2, 117.4, 110.2, 43.7, 29.6, 21.2, 19.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_2O$: 355.1798, found: 355.1805; IR (KBr): 3853, 3701, 1716, 1601, 1560, 1459, 1443, 1421, 1358, 1241, 1166, 829, 775, 745, 703 cm^{-1}.

4-(1-(5-Chloropyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-2-one (3p): colorless solid; 31 mg, 42% yield; m.p. 150.2–152.1 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 2.6 Hz, 1H), 7.93 (dd, J = 8.5, 2.6 Hz, 1H), 7.61 (dd, J = 7.1, 1.3 Hz, 1H), 7.55–7.48 (m, 5H), 7.42–7.37 (m, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.21 (m, 2H), 3.21 (dd, J = 8.7, 7.0 Hz, 2H), 2.63–2.55 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.2, 149.6, 148.6, 138.4, 136.5, 135.8, 134.5, 130.4, 129.9, 128.7, 128.4, 126.8, 122.8, 121.9, 121.4, 119.4, 118.1, 110.1, 43.6, 29.7, 19.6; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{20}ClN_2O$: 375.1252, found: 375.1259; IR (KBr): 3505, 1713, 1647, 1395, 1354, 1188, 1111, 1012, 771 cm^{-1}.

4-(1-(5-Bromopyridin-2-yl)-3-phenyl-1H-indol-2-yl)butan-2-one (3q): colorless solid; 20 mg, 24% yield; m.p. 160.3–

163.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, J = 2.1 Hz, 1H), 8.07 (dd, J = 8.4, 2.5 Hz, 1H), 7.61 (dd, J = 7.1, 1.3 Hz, 1H), 7.55–7.46 (m, 5H), 7.41–7.35 (m, 2H), 7.25–7.17 (m, 2H), 3.22 (dd, J = 8.7, 7.0 Hz, 2H), 2.63–2.56 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.2, 150.8, 150.0, 141.2, 136.5, 135.8, 134.5, 129.9, 128.7, 128.5, 126.8, 122.8, 122.4, 121.4, 119.4, 118.7, 118.2, 110.0, 43.6, 29.7, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{20}BrN_2O$: 419.0745, found: 419.0754; IR (KBr): 3648, 3612, 3566, 1747, 1713, 1465, 1361, 1189, 836, 742, 702 cm^{-1}.

4-(3-Phenyl-1-(5-(trifluoromethyl)pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3 r): yellow solid; 35 mg, 43% yield; m.p. 143.5–145.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.19 (dd, J = 8.4, 2.2 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.64–7.60 (m, 1H), 7.57–7.49 (m, 4H), 7.46 (d, J = 7.4 Hz, 1H), 7.41 (m, 1H), 7.24 (m, 2H), 3.32–3.20 (m, 2H), 2.66–2.56 (m, 2H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 154.2, 146.9 (q, J = 4.0 Hz, $^{3}J_{CF}$), 136.3, 135.9, 135.9 (q, J = 6.1 Hz, $^{3}J_{CF}$), 134.3, 129.9, 128.9, 128.8, 127.0, 124.6 (q, J = 27.3 Hz, $^{2}J_{CF}$), 123.4 (d, J = 279.8 Hz, $^{1}J_{CF}$), 123.1, 121.8, 120.4, 119.5, 119.1, 110.1, 43.6, 29.6, 19.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{20}F_3N_2O$: 409.1522, found: 409.1522; IR (KBr): 3866, 3612, 2308, 1867, 1713, 1465, 1375, 1189, 836, 770, 742, 703 cm^{-1}.

Methyl 4-(2-(3-oxobutyl)-1-(pyridin-2-yl)-1H-indol-3-yl) butanoate (5 c): yellow oil; 31 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.7 Hz, 1H), 7.92 (m, 1H), 7.63–7.56 (m, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 10.5, 5.4 Hz, 2H), 7.21–7.11 (m, 2H), 3.69 (s, 3H), 3.16–3.04 (m, 2H), 2.87–2.76 (m, 2H), 2.72–2.61 (m, 2H), 2.44 (t, J = 7.3 Hz, 2H), 2.07 (s, 3H), 2.05–1.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 174.1, 151.5, 149.7, 138.4, 136.7, 135.9, 128.6, 122.1, 122.0, 121.0, 120.4, 118.6, 114.1, 110.0, 51.5, 43.8, 33.7, 29.8, 25.8, 23.6, 19.3; HR-MS (ESI) calcd for $[M+H]^+$: $C_{22}H_{25}N_2O_3$: 365.1860, found: 365.1856; IR (KBr): 3649, 3553, 1747, 1705, 1689, 1681, 1647, 1567, 1516, 1266, 899, 742 cm^{-1}.

1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)pentan-3-one (6 a): colorless solid; 50 mg, 71% yield; m.p. 87.4–89.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.6 Hz, 1H), 7.96 (t, J = 7.7 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.58–7.54 (m, 3H), 7.51 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.6 Hz, 3H), 7.24–7.17 (m, 2H), 3.29–3.21 (m, 2H), 2.58–2.52 (m, 2H), 2.22 (q, J = 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 151.4, 149.8, 138.6, 136.7, 136.1, 134.8, 129.9, 128.7, 128.3, 126.6, 122.5, 122.4, 121.4, 121.1, 119.2, 117.6, 110.1, 42.1, 35.6, 19.8, 7.8; HR-MS (ESI) calcd for $[M+H]^+$: $C_{24}H_{23}N_2O$: 355.1805, found: 355.1803; IR (KBr): 3734, 3489, 1713, 1660, 1647, 1586, 1470, 1457, 1436, 1371, 1318, 1236, 1189, 771, 742, 703 cm^{-1}.

1-Cyclohexyl-3-(3-phenyl-1-(pyridin-2-yl)-1H-inden-2-yl) propan-1-one (6 b): colorless solid; 70 mg, 86% yield; m.p. 92.4–93.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 3.8 Hz, 1H), 7.95 (m, 1H), 7.68–7.63 (m, 1H), 7.60–7.55 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H), 7.39 (dd, J = 12.2, 5.3 Hz, 3H), 7.25–7.16 (m, 2H), 3.23 (dd, J = 10.4, 5.5 Hz, 2H), 2.71–2.56 (m, 2H), 2.14 (s, 1H), 1.68 (d, J = 24.7 Hz, 5H), 1.19 (d, J = 4.0 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.6, 151.4, 149.8, 138.6, 136.8, 136.4, 134.9, 129.9, 128.7, 128.3, 126.6, 122.5, 122.4, 121.5, 121.1, 119.2, 117.5, 110.1, 50.5, 40.5, 28.4, 25.8, 25.6, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{28}H_{29}N_2O$: 409.2274, found: 409.2263; IR (KBr): 3819, 3648, 2929, 2852, 1705, 1586, 1470, 1371, 1318, 1147, 988, 771, 742, 702 cm^{-1}.

1-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)octan-3-one (6 c): yellow oil; 59 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.4 Hz, 1H), 7.96 (t, J = 7.7 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.60–7.54 (m, 3H), 7.51 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.3 Hz, 3H), 7.25–7.16 (m, 2H), 3.32–3.16 (m, 2H), 2.59–2.49 (m, 2H), 2.19 (t, J = 7.4 Hz, 2H), 1.45 (dd, J = 15.0, 7.5 Hz, 2H), 1.28–1.22 (m, 2H), 1.19–1.12 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 151.4, 149.8, 138.6, 136.7, 136.1, 134.8, 129.9, 128.7, 128.3, 126.6, 122.5, 122.4, 121.4, 121.1, 119.2, 117.6, 110.1, 42.5, 31.3, 23.6, 22.4, 19.7, 13.9; HR-MS (ESI) calcd for $[M+H]^+$: $C_{27}H_{29}N_2O$: 397.2274, found: 397.2269; IR (KBr): 3901, 3672, 2929, 2862, 1748, 1714, 1682, 1471, 1371, 1266, 1189, 770, 741, 703 cm^{-1}.

1-Phenyl-4-(3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (6 d): brown oil; 66 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 3.8 Hz, 1H), 7.90 (m, 1H), 7.62 (d, J = 6.9 Hz, 1H), 7.52–7.44 (m, 5H), 7.38 (dd, J = 8.7, 3.8 Hz, 1H), 7.33 (t, J = 6.6 Hz, 2H), 7.27 (d, J = 8.7 Hz, 3H), 7.23–7.15 (m, 2H), 7.08–6.94 (m, 2H), 3.49 (s, 2H), 3.25–3.12 (m, 2H), 2.68–2.56 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 151.3, 149.8, 138.5, 136.7, 135.9, 134.7, 134.1, 129.9, 129.3, 128.7, 128.7, 128.2, 127.0, 126.6, 122.6, 122.4, 121.3, 121.1, 119.2, 117.6, 110.1, 49.9, 41.9, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{29}H_{25}N_2O$: 417.1961, found: 417.1951; IR (KBr): 3500, 3055, 2922, 1714, 1644, 1494, 1470, 1370, 1236, 1187, 743, 700 cm^{-1}.

1-Phenyl-5-(3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)pentan-3-one (6 e): colorless solid; 75 mg, 87% yield; m.p. 84.6–85.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 3.9 Hz, 1H), 7.95 (t, J = 7.2 Hz, 1H), 7.65 (d, J = 7.1 Hz, 1H), 7.53 (dd, J = 17.0, 7.7 Hz, 5H), 7.43–7.35 (m, 3H), 7.26 (dd, J = 17.9, 10.6 Hz, 5H), 7.10 (d, J = 7.1 Hz, 2H), 3.31–3.20 (m, 2H), 2.78 (t, J = 7.5 Hz, 2H), 2.55 (dd, J = 17.3, 9.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 151.3, 149.8, 140.9, 138.7, 138.6, 136.7, 135.9, 134.8, 129.9, 128.7, 128.5, 128.3, 126.6, 126.1, 122.6, 122.4, 121.4, 121.1, 119.2, 117.6, 110.1, 44.0, 42.7, 29.7, 19.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{30}H_{27}N_2O$: 431.2118, found: 431.2110; IR (KBr): 3905, 3598, 1712, 1654, 1560, 1470, 1370, 1319, 1192, 1094, 771, 744, 701 cm^{-1}.

4-Phenyl-1-(3-phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)pentan-3-one (6 f): yellow oil; 59 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.6 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.52–7.43 (m, 4H), 7.42 (d, J = 8.0 Hz, 1H), 7.39–7.33 (m, 1H), 7.34–7.23 (m, 5H), 7.23–7.15 (m, 2H), 7.07–6.99 (m, 2H), 3.56 (q, J = 6.9 Hz, 1H), 3.31–3.18 (m, 1H), 3.18–3.02 (m, 1H), 2.67–2.42 (m, 2H), 1.30 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 151.2, 149.7, 140.5, 138.4, 136.7, 136.0, 134.7, 129.8, 128.9, 128.6, 128.2, 127.7, 127.0, 126.5, 122.5, 122.3, 121.2, 121.0, 119.2, 117.5, 110.1, 52.7, 41.0, 19.9, 17.2; HR-MS (ESI) calcd for $[M+H]^+$: $C_{30}H_{27}N_2O$: 431.2118, found: 431.2104; IR (KBr): 3571, 3055, 2973, 2930, 1713, 1601, 1493, 1318, 1286, 1023, 990, 771, 744 cm^{-1}.

(*E*)-4-(3-Phenyl-1-(pyridin-2-yl)-1H-indol-2-yl)but-3-en-1-ol (6 h): yellow oil; 26 mg, 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 3.9 Hz, 1H), 7.93 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 7.1 Hz, 1H), 7.57 (d, J = 7.5 Hz, 2H), 7.51 (dd, J = 12.7, 7.7 Hz, 3H), 7.42–7.35 (m, 3H), 7.25–7.17 (m, 2H), 5.59–5.19 (m, 2H), 3.86–3.76 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 149.7, 138.3, 136.9, 134.8, 134.5, 130.5, 130.0, 129.3, 128.5, 128.0, 126.5, 122.6, 122.4, 121.6, 121.0, 119.3, 117.9, 110.0, 63.2, 28.2; HR-MS (ESI) calcd for $[M+H]^+$: $C_{23}H_{20}N_2O$: 341.1648, found: 341.1640; IR (KBr): 3929, 3825, 3082, 2906, 1583, 1507, 1375, 1190, 1087, 745, 702 cm^{-1}.

Procedure for the Synthesis of Compounds 3 g, 3 h, 5 a and 5 b

An oven-dried sealed tube charged **1** or **4**(0.20 mmol), **2 a** (0.40 mmol), $AgSbF_6$ (20 mol%), $[Cp^*RhCl_2]_2$ (5 mol%), and H_2O (1.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at 85 °C for 24 h. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:10 ~ 1:5) as eluent to afford the desired products **3** or **5**.

4-(3-Methyl-1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3 g): brown oil; 43 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, J = 4.8, 1.3 Hz, 1H), 7.91 (m, 1H), 7.57 (dd, J = 5.6, 3.3 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.36–7.29 (m, 2H), 7.22–7.12 (m, 2H), 3.14 (dd, J = 9.9, 5.7 Hz, 2H), 2.70 (dd, J = 10.1, 5.5 Hz, 2H), 2.35 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 151.6, 149.6, 138.4, 136.5, 135.5, 129.4, 122.1, 121.8, 120.8, 120.4, 118.4, 110.3, 109.9, 43.5, 29.9, 19.5, 8.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{18}H_{19}N_2O$: 279.1492, found: 279.1494; IR (KBr): 3455, 2921, 1714, 1586, 1471, 1459, 1437, 1362, 1317, 1224, 1163, 993, 777, 741 cm^{-1}.

4-(1-(Pyridin-2-yl)-1H-indol-2-yl)butan-2-one (3 h): yellow oil; 34 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 4.8, 1.2 Hz, 1H), 7.92 (m, 1H), 7.59 (m, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.35 (dd, J = 7.8, 4.8 Hz, 2H), 7.16 (dd, J = 6.0, 3.1 Hz, 2H), 6.45 (s, 1H), 3.15–3.09 (m, 2H), 2.88–2.83 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 151.3, 149.7, 140.0, 138.5, 137.3, 128.5, 122.2, 121.9, 121.1, 120.8, 120.1, 110.2, 102.3, 42.8, 30.0, 21.7; HR-MS (ESI) calcd for $[M+H]^+$: $C_{17}H_{17}N_2O$: 265.1335, found: 265.1335; IR (KBr): 3738, 3005, 1713, 1469, 1456, 1436, 1344, 1266, 1212, 917, 741 cm^{-1}.

10-(2-(3-Oxobutyl)-1-(pyridin-2-yl)-1H-indol-3-yl)decanal (5 a): yellow oil; 38 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.66–8.59 (m, 1H), 7.91 (m, 1H), 7.61–7.55 (m, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 (m, 2H), 7.16 (m, 2H), 3.16–3.07 (m, 2H), 2.80–2.73 (m, 2H), 2.70–2.60 (m, 2H), 2.43 (m, 2H), 2.06 (s, 3H), 1.72–1.63 (m, 4H), 1.47–1.40 (m, 2H), 1.33 (s, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.8, 203.0, 151.6, 149.6, 138.4, 136.6, 135.4, 128.8, 121.9, 121.9, 120.9, 120.3, 118.6, 115.5, 109.9, 43.9, 30.9, 29.9, 29.8, 29.5, 29.4, 29.2, 24.4, 22.1, 19.4; HR-MS (ESI) calcd for $[M+H]^+$: $C_{27}H_{35}N_2O_2$: 419.2684, found: 419.2693; IR (KBr): 3727, 3628, 2924, 1720, 1587, 1470, 1454, 1437, 1380, 1226, 1099, 740, 697 cm^{-1}.

5-(2-(3-Oxobutyl)-1-(pyridin-2-yl)-1H-indol-3-yl)pentanal (5 b): brown oil; 40 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.64 (d, J = 3.2 Hz, 1H), 7.91 (m, 1H), 7.58–7.54 (m, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.33 (dd, J = 6.8, 4.7 Hz, 2H), 7.19–7.14 (m, 2H), 3.16–3.07 (m, 2H), 2.81 (t, J = 7.0 Hz, 2H), 2.67–2.62 (m, 2H), 2.50 (t, J = 6.2 Hz, 2H), 2.06 (s, 3H), 1.75 (d, J = 5.7 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 202.6, 151.6, 149.7, 138.4, 136.7, 135.6, 128.6, 122.1, 122.0, 120.9, 120.4, 118.5, 114.6, 110.0, 43.9, 43.8, 30.3, 29.9, 24.1, 22.2, 19.3; HR-MS (ESI) calcd for $[M+H]^+$: $C_{22}H_{25}N_2O_2$: 349.1911, found: 349.1912; IR (KBr): 3839, 3650, 3612, 3565, 1867, 1747, 1705, 1689, 1515, 1266, 905, 742 cm^{-1}.

Chemical Transformation of 3 h

Coupling-cyclization of **3 h** with ethyl carbonocyanidate:[14] To a mixture of **3 h** (106 mg, 0.4 mmol) and Et_3N (4 mg, 0.04 mmol), ethyl carbonocyanidate **7** (44 mg, 0.44 mmol) was slowly added at rt. Upon completion, the reaction was concentrated in vacuum. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether = 5:1) to give product **8** (76 mg, 52% yield).

A mixture of substrate **8** (73 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 5 mol%) and 2,2′-bipyridine (2 mg, 6 mol%) in HOAc/NMA (v/v = 1/3, 0.5 mL) was stirred at 120 °C. Upon completion, the mixture was cooled to room temperature, and then $NaHCO_3$ was added until no CO_2 bubbles were generated. The resulting mixture was extracted with DCM three times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc (3:1 to 1:1) as the eluent to give the desired product **9** (50 mg, 79% yield).

2-Cyano-4-(1-(pyridin-2-yl)-1H-indol-2-yl)butan-2-yl ethyl carbonate (8): colorless oil; 76 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.9, 1.2 Hz, 1H), 7.94 (m, 1H), 7.66–7.57 (m, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.41–7.31 (m, 2H), 7.21–7.14 (m, 2H), 6.52 (s, 1H), 4.28–4.19 (m, 2H), 3.17 (m, 2H), 2.36 (m, 2H), 1.78 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 151.1, 149.8, 138.7, 138.5, 137.1, 128.4, 122.2, 122.2, 120.9, 120.7, 120.2, 118.1, 110.2, 103.1, 73.5, 64.9, 39.2, 24.5, 22.4, 14.1; HR-MS (ESI) calcd for $[M+H]^+$: $C_{21}H_{22}N_3O_3$: 364.1653, found: 364.1656; IR (KBr): 2951, 1753, 1456, 1389, 1214, 1017, 673, 579 cm^{-1}.

3 a-Methyl-6-(pyridin-2-yl)-3 a,4,5,6-tetrahydro-2H-oxazolo [5,4-c]carbazol-2-one (9): yellow oil; 50 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 3.3 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 8.04 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.49 (dd, J = 12.1, 7.5 Hz, 2H), 7.43–7.34 (m, 2H), 3.48–3.34 (m, 1H), 3.10 (dd, J = 18.6, 5.4 Hz, 1H), 2.54 (dd, J = 12.4, 5.1 Hz, 1H), 2.28 (dd, J = 12.1, 6.0 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 167.7, 150.1, 149.3, 149.1, 139.1, 138.1, 124.9, 124.1, 123.7, 121.8, 120.2, 111.2, 107.7, 85.3, 34.5, 29.7, 23.1, 23.1; HR-MS (ESI) calcd for $[M+H]^+$: $C_{19}H_{16}N_3O_2$: 318.1232, found: 318.1237; IR (KBr): 3728, 3628, 2930, 1583, 1456, 1380, 1162, 1078 cm^{-1}.

Coupling-cyclization of 3-1 h with methyl 2-diazo-2-phenylacetate:[15] To an oven-dried sealed tube charged **3 h**

(53 mg, 0.20 mmol), **10** (70 mg, 0.40 mmol), $Rh_2(OAc)_4$ (3 mg, 5 mol%) and CH_2Cl_2 (1.5 mL) was added under Ar atmosphere. The reaction mixture was then allowed to stir at 40 °C for 1 h. The corresponding reaction mixture was then cooled down and filtrated. The corresponding filtrate was further concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:10 ~ 1:5) as eluent to afford the desired products **11** (59 mg, 72% yield).

Methyl-3-hydroxy-3-methyl-4-phenyl-9-(pyridin-2-yl)-2,3,4,9-tetrahydro-1H-carbazole-4-carboxylate (11): yellow oil; 59 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 4.8, 1.1 Hz, 1H), 7.94 (m, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.39–7.29 (m, 4H), 7.26 (s, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.9 Hz, 1H), 6.98 (t, J = 7.3 Hz, 1H), 4.69 (s, 1H), 3.63 (s, 3H), 3.19–3.02 (m, 1H), 2.90 (dd, J = 17.6, 4.7 Hz, 1H), 2.74 (m, 1H), 2.04 (dd, J = 12.8, 4.9 Hz, 1H), 0.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 150.9, 149.6, 138.4, 137.4, 137.3, 137.3, 129.8, 127.7, 127.1, 126.9, 123.4, 122.1, 121.8, 120.6, 120.0, 111.5, 110.0, 74.5, 60.6, 52.1, 35.4, 23.4, 22.6; HR-MS (ESI) calcd for $[M+H]^+$: $C_{26}H_{25}N_2O_3$: 413.1854, found: 413.1860; IR (KBr): 2944, 1705, 1587, 1471, 1439, 1361, 1243, 1151, 1041, 910, 738, 443 cm^{-1}.

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