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Catalyst-free Synthesis of 6-Hydroxy Indoles *via* the Condensation of Carboxymethyl Cyclohexadienones and Amines

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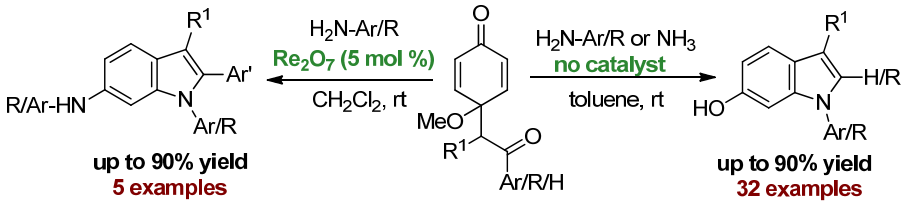


ABSTRACT: An efficient catalyst-free synthesis of 6-hydroxy indoles from carboxymethyl cyclohexadienones and primary amines has been developed. The aza-Michael addition of the in situ formed enamine, generated through the condensation of carboxymethyl unit of the substrates with an external amine, to cyclohexadienone moiety followed by rearomatization reaction to provide such indoles. Anilines, aliphatic amines, α-chiral aliphatic amines or even ammonia were used as amine counterpart. Some of the cyclohexadienones gave 6-amino indoles instead of 6-hydroxy indoles using the Re_2O_7 catalyst. Various post methodological transformations were performed to explore the synthetic utility of the synthesized hydroxy indoles.

INTRODUCTION

Hydroxy indoles are very important skeletons found in many active pharmaceuticals and natural products.[1] 4- and 5-Hydroxyindoles are readily available from commercial sources. However, the synthesis of 6- and 7-hydroxy indoles remained a challenge. They are supplied only in minute amounts from combinatorial libraries. Notably, 6-hydroxy indoles are precious moiety and act as novel protein target inhibitors,[2] use in hair dyes[3] and also are the precursors for the synthesis of numerous other indole alkaloids.[2a-j] For example, JWH 200 (compound **A**, Figure 1) serves as a Cannabinoid receptor agonist,[2a,d] compound **B** is the most promising Fatty acid amide hydrolase (FAAH) inhibitor.[2e] Such moiety is the main precursor for the total synthesis of *Notamide J* (compound **C**).[2f] 6-Hydroxy indole-based BODIPY-OH were also utilized as fluorescent probe in material chemistry.[2i-j] Considering various innovative protocols for the synthesis of C6-functionalized indoles;[4] 6-hydroxy indoles could be an essential intermediate for the synthesis of such C6-functionalized indoles.

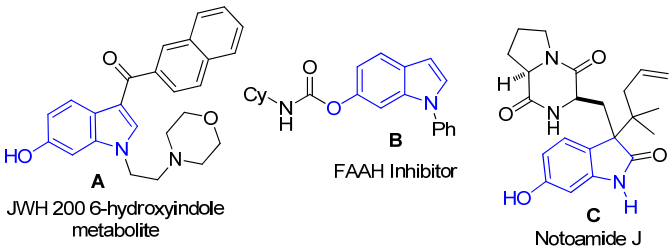
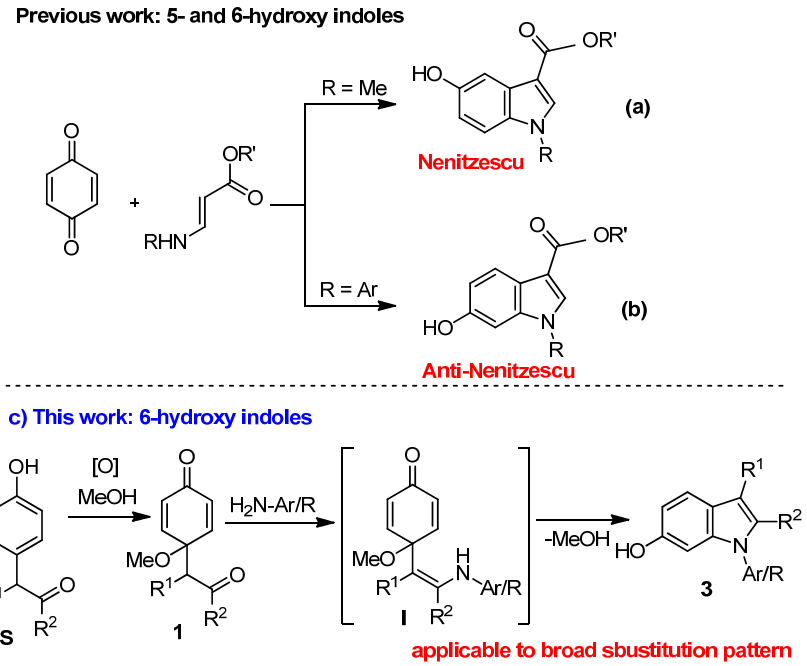


Figure 1. Representative bioactive 6-hydroxy indoles.

A classical and well-established named reaction for the synthesis of hydroxy indole, namely, the Nenitzescu reaction[6a] is limited for the synthesis of 5-hydroxy indoles, regioselectively. It is the condensation of 1,4-benzoquinones with enamines (Scheme 1a).[5,6] On the other hand, regioselective anti-Nenitzescu reaction to provide 6-hydroxy indoles is very rare. For the first time, Grinev observed the formation of 6-hydroxyindoles depends on substitutions of amino-acrylate (on changing substitution form *N*-alkyl to *N*-aryl) on reaction with 1,4-benzoquinones (Scheme 1b).[7a] Lin group also found an anti-Nenitzescu pathway for the synthesis of 3a-hydroxy-indol-6-one.[7e] Other methods for the synthesis of 6-hydroxy indoles remained quite lengthy and very specific regarding substitution pattern.[7b,d]



Scheme 1. Hydroxy indole synthesis from 1,4-benzoquinones: a) synthesis of 5-hydroxy indole (Nenitzescu reaction), b) synthesis of 6-hydroxy indoles (anti-Nenitzescu reaction); this work: c) synthesis of 6-hydroxyindoles from carboxymethyl cyclohexadienones.

Development of the catalyst-free reaction conditions eis always considered to be the ideal,[8] given the purity requirements in the areas of biological and medicinal chemistry.[9] In view of that, the currently

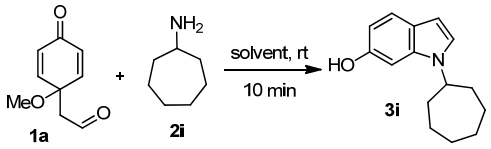
developed method (Scheme 1c) for the synthesis of 6-hydroxy indoles under the catalyst-free reaction conditions would be of high synthetic utility.

Dearomatization of phenol for the synthesis of cyclohexadienones followed by nucleophilic addition reactions on enone moiety remained a captivating approach for the synthesis of complex molecular structures.[10] Our research interest in the further developments in this area[10f] has driven us to design a method for the synthesis of 6-hydroxy indole **3** via the condensation of primary amines with cyclohexadienone **1** having a β-carbonyl moiety attached at 4-position, as depicted in Scheme 1c. The reaction could proceed through the formation of enamine **I** followed by aza-Michael addition and sub-sequent rearomatization reaction. The substrate **1** is synthesized *via* the oxidative dearomatization of the corresponding 4-substituted phenols (**S)** using hypervalent iodine reagents.

RESULTS AND DISCUSSION

We started our initial screening with **1a** and cycloheptylamine (**2i**) in different solvents which are

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

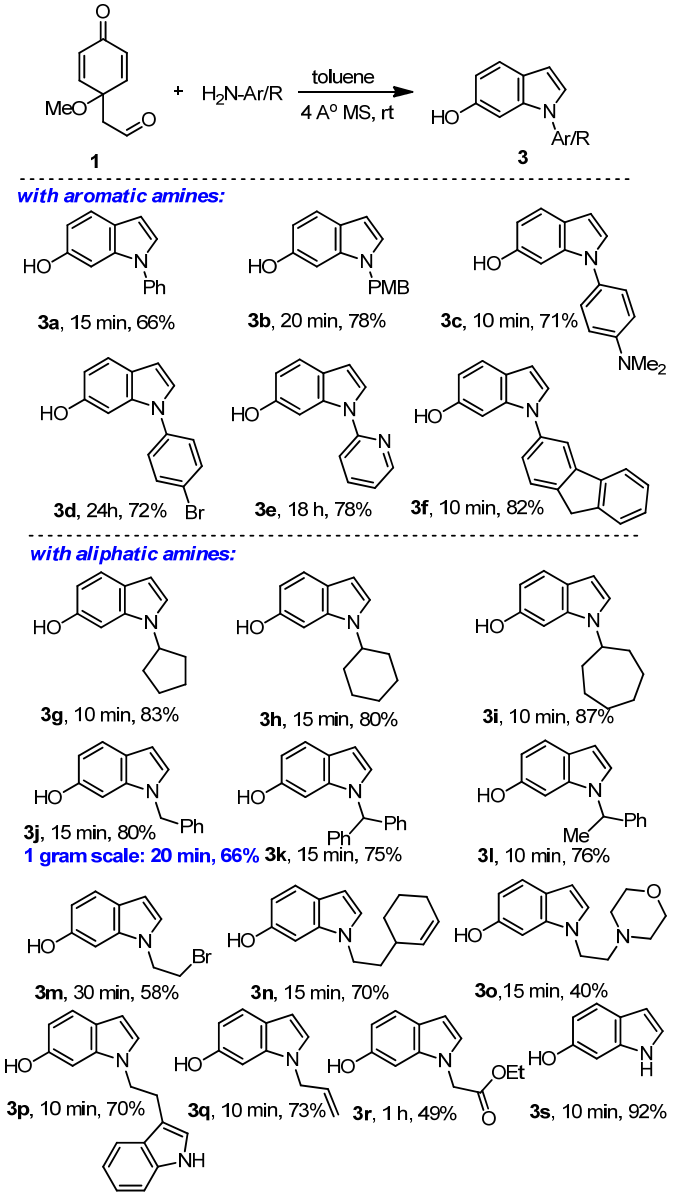


Entry	**2i** (equiv)	Additive	Solvent	Yield (%)
1	1.2	-	CH_2Cl_2	78
2	1.2	-	toluene	82 (83)[c]
3	1.2	-	THF	77
4	1.2	-	CH_3NO_2	54
5	1.2	-	CH_3CN	77
6	1.2	4 A° MS	toluene	87
7	1.2	$MgSO_4$	toluene	75
8	2	-	toluene	87

[a]All the reactions were carried out at **1a** (0.1 mmol, 1 equiv), solvent (0.4 ml). [b]All are isolated yields. [c]Reaction ran at 0 °C.

listed in Table 1 (entries 1-5). Encouragingly, the desired indole **3i** was formed even in the absence of any external catalyst. Toluene remained the best as solvent (entry 2) in term of yield. On decreasing the temperature (to 0 ^{o}C), the slight increase in yield was observed. To accelerate the enamine formation, dehydrating agents such as $MgSO_4$ (entry 7) and 4 A^{o} MS (entry 6) were added. Clearly, an increase in yield of the reaction in case of 4 A^{o} MS (to 87%) was revealed. When the amount of amine **2i** was increased to two equivalents, even without the addition of 4 A^{o} MS a similar yield (entry 8) was obtained.

Scheme 2. Variation of Aryl Amine Counterpart.[a,b]

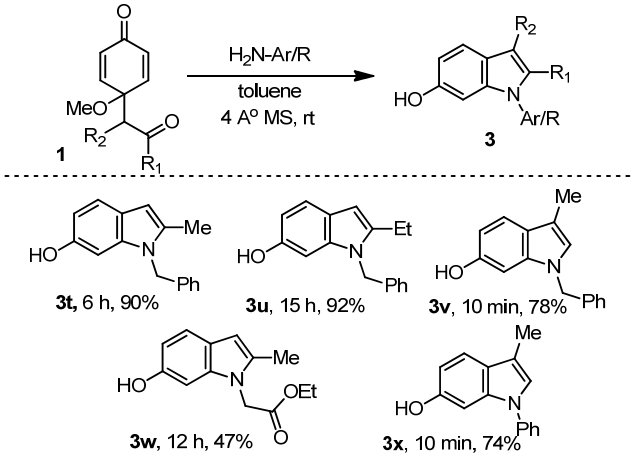


[a]All the reactions were carried out at **1** (0.2 mmol, 1 equiv), amine **2** (0.24 mmol, 1.2 equiv), 4 A^{o} MS, toluene (1.5 ml). [b]All are isolated yields.

With these optimized reaction conditions in hand, different 6-hydroxy indoles were synthesized as shown in Scheme 2. Aryl amines, aniline, *para*-substituted anilines underwent the reaction to provide the desired indoles (**3a-d**) with the good yields (66-78%). 2-Amino pyridine forms indole (**3e**) with 78% yield under the similar reaction conditions. The bulky amine such as fluorenyl amine (**2f**) also provided an excellent yield (**82%**) of 6-hydroxy indole **3f**. After this, we turned our attention towards the aliphatic amines. Cycloalkyl amines such as cyclopentyl (**3g**, 83%), cyclohexyl (**3h**, 80%), cycloheptyl (**3i**, 87%); benzylamines such as benzyl (**3j**, 80%), 1-phenyl-benzyl (**3k**, 75%), 1-methyl-benzyl (**3k**, 78%) amines provided very good yields of corresponding 6-hydroxy indoles. Acyclic amines such as 2-bromoethyl amine (**3m**, 60%), 2-cyclohexenyl ethyl amine (**3n**, 70%), morpholinyl N-ethyl amine (**3o**, 40%), tryptamine (**3p,** 70%), allyl amine (**3q**, 73%) and α-aminoester (**3r**, 49%) also worked smoothly to provide the desired indoles. Notably, morpholinyl N-ethyl protected 6-hydroxy indole (**3o**) can further be transformed into JWH 200,[2d] a Cannabinoid receptor agonist. More interestingly, simple ammonia (1M solution in dioxane) reacted with **1a** to give unsubstituted 6-hydroxy indole (**3s**) with excellent yield (92%). Further, to showcase the practical viability of our methodology, the reaction was performed at one gram scale for the synthesis of **3j** and ended up with 66% of the product yield.

Then, we turned our focus to synthesize the substituted hydroxy indoles which are summarized in Scheme 3. Interestingly, substitution of alkyl groups (Me and Et) at 2- as well as 3-position were well tolerated as shown in the case of indoles **3t**-**x**.

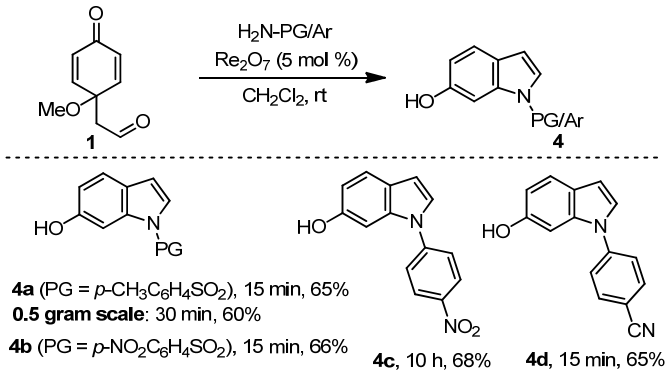
Scheme 3. Variation of Carbonyl Counterpart.[a,b]



[a]Reaction conditions are same as Scheme 2. [b]All are isolated yields.

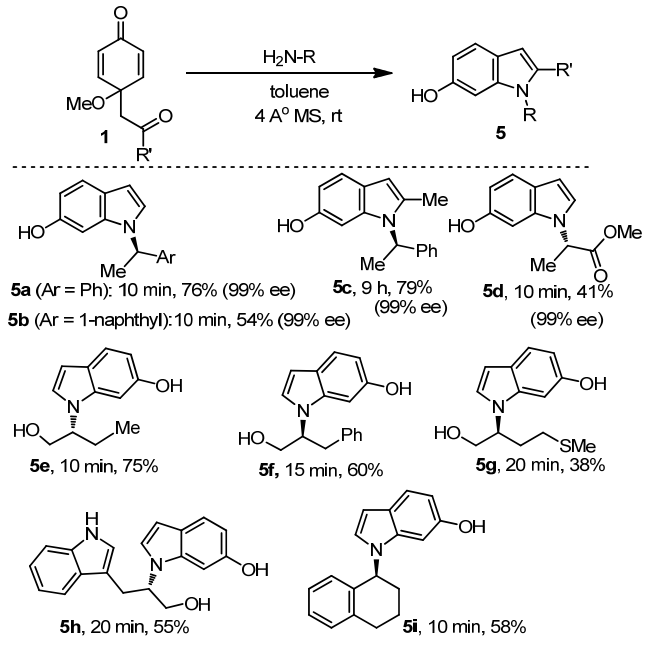
After successful utilization of aryl and alkyl amines, we desired to explore the amines with electron-deficient substitutions. Unfortunately, under the optimized reaction conditions, the desired indoles were not formed. Probably, the enamine formation was unfavorable or aza-Michael addition was not feasible. To overcome this, the reaction was carried out in the presence of catalytic Lewis acid such as Re_2O_7 (5 mol %). To our delight, the desired indoles were obtained in good yields (Scheme 4). Sulfonylamines (**4a-b**) and 4-nitro- and 4-cyano-anilines (**4c** and **4d**, respectively) gave the good yields (65-70%) of the corresponding 6-hydroxy indoles. Even, **4a** was prepared 0.5g scale with 60% yield.

Scheme 4. Electron-deficient Amines.[a,b]



[a]All are reactions were carried out at **1** (0.2 mmol, 1 equiv), amine **2** (0.24 mmol, 1.2 equiv), Re_2O_7 (5 mol%), CH_2Cl_2 (1.5 ml), rt. [b]All are isolated yields.

Scheme 5. Variation of Amines: α-Chiral Amines[a,b,c]

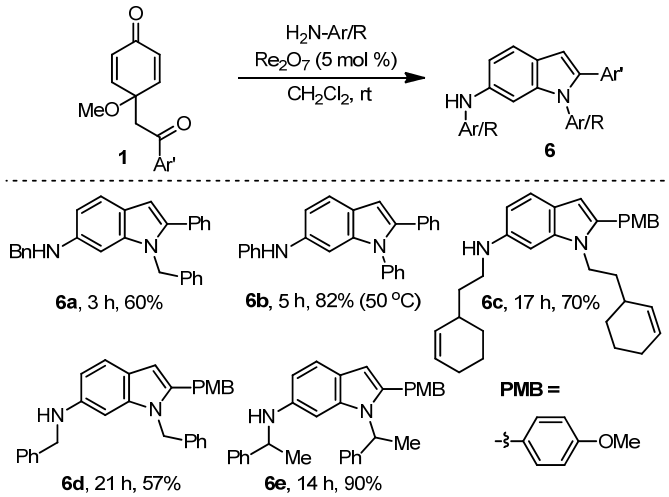


[a]Reaction conditions are same as Scheme 2. [b]All are isolated yields.[c]The ee's were determined by chiral HPLC analysis.

Further, we aimed towards the synthesis of optically active 6-hydroxy indoles using enantioenriched amines as substrate (Scheme 5). Under the catalyst-free reaction conditions, various chiral α-methyl benzylamines gave the corresponding indoles (**5a-c**) with moderate to good yields (54-79%). Similarly, methyl ester of L-alanine gave the product (**5d**) with acceptable yield. Unlike alanine, methyl ester of other aminoacids didn't give the desired product. However, on the use of aminol (reduced product of amino acid), the reaction underwent smoothly to get the corresponding indoles (**5e-h**). Finally, on reaction with tetrahydronaphthylamine also gave the desired product (**5i**) with good yield. Nevertheless, this is the very first method for the direct synthesis of enantioenriched N-alkylated 6-hydroxyindoles from chiral amine counterpart.[11]

To our surprise, when the reaction was performed with aryl ketones instead of alkyl one, the formation of unusual 6-aminoindoles (**6a-e**) was observed (Scheme 6). Probably, the formation of iminium ion on the cyclohexadienone moiety is faster compared to the enamine formation on the aryl ketone. Thus, the aza-Michael addition of enamine to the conjugated iminium ion leads to the formation of 6-aminoindoles. To the best of our knowledge, this is also the first method to access such amino-indoles precisely.

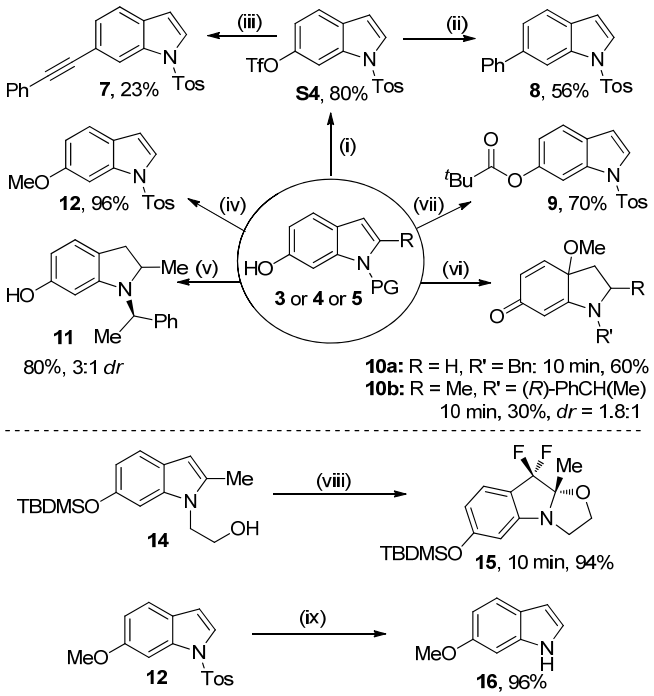
Scheme 6. Synthesis of 6-Amino Indoles[a,b]



[a]All are reactions were carried out at **1** (0.2 mmol, 1 equiv), amine **2** (0.44 mmol, 2.2 equiv), Re_2O_7 (5 mol%), CH_2Cl_2 (1.5 ml), rt. [b]All are isolated yields.

Further, to explore the synthetic utility of our methodology, functionalization of the synthesized 6-hydroxy indoles were performed (Scheme 7). First, the conversion of hydroxy group of 6-hydroxy indole into the corresponding triflate followed by Pd-catalyzed coupling with phenyl boronic acid as well as phenylacetylene gave 6-phenyl (**8)** and 6-ethynylphenyl (**7**) indoles, respectively. Esterification of 6-hydroxy group with pivaloyl chloride leads to the formation of 1-tosyl-1*H*-indol-6-yl pivalate (**9**). The reduction of indole to 2,3-dihydroindole followed by dearomatization using PIDA forms tetrahydro-6*H*-indol-6-one moiety (**10**) which is an important structural core of many natural products.[12] Similarly, reduction of chiral 1-alkyl-6-hydroxyindole to indoline (**11**) moiety with sodium cyanoborohydride ended up with **3:1** diastereoselectivity. Methylation of **4a** formed 6-methoxy indole (**12**) in good yield. Interestingly, a N-hydroxy ethyl indole **14** furnished the corresponding tricyclic N,O-heterocycle **15** under dearomative fluorocyclization pathway. Finally, the tosyl group was deprotected to get 6-methoxy indole (**16**) in good yield.

Scheme 7. Synthetic Elaborations[a, b]



[a]Reaction conditions: (i) **4a** (0.2 mmol), triethylamine (0.4 mmol, 2 equiv), $(Tf)_2O$ (0.3 mmol, 1.5 equiv), CH_2Cl_2 (1.5 ml), -40 ^oC, 2 h. (ii) $PhB(OH)_2$ (0.24 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (5 mol %), $Ba(OH)_2$ (0.4 mmol, 2 equiv), DME:H_2O (2:1 v/v, 3 ml), 90 ^oC, 18 h. (iii) phenylacetylene (0.24 mmol,

1.2 equiv), $Pd(OAc)_2$ (5 mol %), K_3PO_4 (0.22 mmol, 1.1 equiv), PPh_3 (20 mol %), DMSO (1.5 ml), 80 ^oC, 24 h. (iv) **4a** (0.2 mmol), NaH (0.24 mmol, 1.2 equiv), MeI (0.24 mmol, 1.2 equiv) and THF (2 ml). (v) **5c** (0.2 mmol), $NaCNBH_3$ (0.64 mmol, 3.2 equiv), CH_3CO_2H (1.5 ml), rt, 2 h. (vi) (a) same as condition (v); (b) $PhI(OAc)_2$ (0.24 mmol, 1.2 equiv), MeCN:MeOH (9:1 v/v, 1 ml), 10 min. (vii) **4a** (0.15 mmol), triethylamine (0.16 mmol, 1.5 equiv), DMAP (0.01 mmol, 0.1 equiv), trimethylacetylchloride (0.16 mmol, 1.5 equiv), CH_2Cl_2 (1.5 ml), rt, 2 h. (viii) **14** (0.1 mmol), selectfluor (0.2 mmol, 2 equiv), $NaHCO_3$ (0.1 mmol, 1 equiv) and MeCN, 0 ^oC. (ix) **12** (0.2 mmol), Mg granules (3.6 mmol), MeOH (2 ml), sonicated for 1.5 h, rt. [b]All are isolated yields

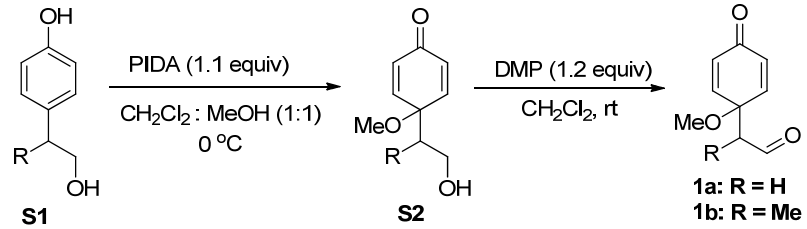
CONCLUSIONS

In summary, a catalyst-free method for the regiospecific synthesis of 6-hydroxy indoles has been developed *via* the condensation of carboxymethyl cyclohexadienones and amines. The substrate scope was quite broad including aromatic, aliphatic and α-chiral amines. Various synthetic transformations from the synthesized hydroxy indoles were also performed successfully. Overall, the methodology is promising and operationally simple for the synthesis of 6-hydroxy indole core which is widely found in pharmaceuticals and natural products.

EXPERIMENTAL SECTION

General Remarks: All reagents and solvents were used as supplied commercially. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated Science silica gel (EM 60-F254) plates. Visualization was accomplished with UV light (254 nm) and exposure to either ethanolic phosphomolybdic acid (PMA), anisaldehyde or $KMnO_4$ solution, $CeSO_4$ + ammonium phosphomolybdate + 10% H_2SO4 followed by heating. Melting points are uncorrected. ^1H NMR spectra were acquired on 400 MHz or 500 MHz spectrometers. ^{13}C NMR spectra were obtained on 100 MHz or 125 MHz spectrometers. Chemical shifts are reported in ppm relative to the residual solvent peak. Unless noted, NMR spectra were acquired in $CDCl_3$ or DMSO-D_6; individual peaks are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant in Hz. All IR spectra were obtained as neat films, and selected absorbances are reported in cm^{-1}. Low-resolution mass spectrometry data were acquired by GC-MS (EI 70 eV) using DB-5 column. High-resolution data were acquired using a MicroTOF-Q-II Mass Spectrometer in MeOH as a solvent or using GC-QTOF Mass Spectrometer.

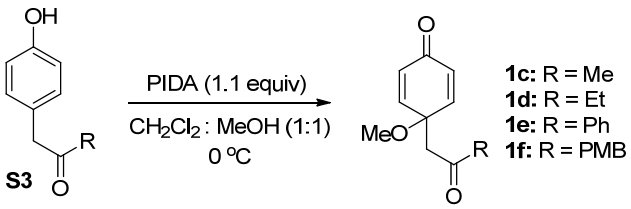
Materials: The starting materials **S1** and amines were acquired from commercial sources. Starting materials **S2, S3, 1C** and few chiral amines were prepared according to the reported procedures.[13] Remaining compounds **1a**, **1b**, **1d**, **1e** and **1f** were prepared by using the following reported procedures.[13]



General procedure for the synthesis of starting material (**1a-b**): To a stirred solution of **S2** (10 mmol, 1 equiv) in dichloromethane (25 mL) at 0 °C, Dess-Martin Periodinane (12 mmol, 1.2 equiv) was added portion wise. The reaction mixture was stirred for 2 h at room temperature. After completion of the starting material (monitored by TLC), the reaction mixture was quenched with $Na_2S_2O_3$ solution and extracted with dichloromethane (3 x 10 mL). The combined organic layers were washed with brine followed by dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. Finally, the crude residue was purified by flash column chromatography (EtOAc/n-Hexane) on silica-gel to provide **1a-b.**

2-(1-Methoxy-4-oxocyclohexa-2,5-dien-1-yl)acetaldehyde (**1a**): 913 mg, 55% yield; R_f = 0.52 (30:70 = EtOAc/n-Hexane); Brown colored liquid; **FT-IR (neat)**: 2932, 2360, 2329, 1715, 1629, 1520, 1459, 1276, 1246, 1083, 862 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 9.75 (t, *J* = 2.6 Hz, 1H), 6.84 (d, *J* = 10.3 Hz, 2H), 6.39 (d, *J* = 10.3 Hz, 2H), 3.20 (s, 3H), 2.68 (d, *J* = 2.6 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 198.4, 184.5, 148.6, 131.9, 73.4, 53.1, 51.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_9H_{11}O_3$: 167.0703; found: 167.0712.

2-(1-Methoxy-4-oxocyclohexa-2,5-dien-1-yl)propanal (**1b**): 147 mg, 41% yield; R_f = 0.43 (20:80 = EtOAc/n-Hexane); Light yellow colored liquid; **FT-IR (neat)**: 3054, 2931, 2363, 2333, 1728, 1673, 1267, 1083, 853, 738 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 9.90 (s, 1H), 6.71 (ddd, *J* = 15.7, 9.9, 2.9 Hz, 2H), 6.42 (t, *J* = 10.4 Hz, 2H), 3.21 (s, 3H), 2.79 (tt, *J* = 7.0, 3.6 Hz, 1H), 0.99-0.85 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 202.2, 184.7, 148.6, 146.9, 133.2, 132.5, 77.6, 53.2, 52.6, 8.9; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{10}H_{13}O_3$: 181.0859; found: 181.0861.



General procedure for the synthesis of starting material (**1c-f**): To a stirred solution of **S3** (2.0 mmol, 1 equiv) in methanol (4 mL) at 0 °C, (diacetoxy)iodobenzene (2.4 mmol, 1.2 equiv), dissolved in dichloromethane (4 mL), was added drop wise over a period of 2 h using syringe pump. The reaction mixture was stirred for 30 min at room temperature. After complete consumption of the starting material (monitored by TLC), the solvents were evaporated under reduced pressure. Finally, the crude reaction mixture was purified by column chromatography (EtOAc/n-Hexane) over silica-gel to give pure products **1d-f**.

4-Methoxy-4-(2-oxobutyl)cyclohexa-2,5-dien-1-one (**1d**): 131 mg, 34% yield; R_f = 0.26 (20:80 = EtOAc/n-Hexane); Light yellow colored liquid; **FT-IR (neat)**: 3057, 2979, 2938, 2829, 2354, 1715, 1673, 1634, 1515, 1456, 1379, 1274, 1091, 861, 736 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 6.87 (d, *J* = 10.2 Hz, 2H), 6.31 (d, *J* = 10.1 Hz, 2H), 3.11 (s, 2H), 2.68 (s, 3H), 2.48 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 207.0, 185.1, 149.5, 131.2, 73.4, 53.0, 50.7, 38.8, 7.4; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{11}H_{15}O_3$: 195.1016; found: 195.1008.

4-Methoxy-4-(2-oxo-2-phenylethyl)cyclohexa-2,5-dien-1-one (**1e**): 251 mg, 52% yield; R_f = 0.54 (30:70 = EtOAc/n-Hexane); Yellow colored solid; mp: 73-75 °C; **FT-IR (neat)**: 3061, 2937, 2829, 2316, 1674, 1631, 1452, 1074, 860, 754 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 8.02-7.85 (m, 2H), 7.63-7.51 (m, 1H), 7.53-7.37 (m, 2H), 7.04-6.90 (m, 2H), 6.47-6.28 (m, 2H), 3.31 (s, 2H), 3.17 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 195.7, 185.2, 149.4, 137.6, 133.4, 131.4, 128.6, 128.6, 73.6, 52.9, 47.0; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{15}H_{15}O_3$: 243.1016; found: 243.1025.

4-Methoxy-4-(2-(4-methoxyphenyl)-2-oxoethyl)cyclohexa-2,5-dien-1-one (**1f**): 261 mg, 48% yield; R_f = 0.29 (20:80 = EtOAc/n-Hexane); Yellow colored semi solid; **FT-IR (neat)**: 2937, 2833, 1672, 1598, 1259, 1172, 1070, 858 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 8.02-7.79 (m, 2H), 7.05-6.76 (m, 4H), 6.46-6.25 (m, 2H), 3.91-3.77 (m, 3H), 3.26 (d, *J* = 1.8 Hz, 2H), 3.16 (d, *J* = 2.3 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 194.1, 185.2, 163.8, 149.6, 131.3, 131.0, 130.6, 113.7, 73.7, 55.5, 52.8, 46.8; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{16}H_{17}O_4$: 273.1121; found: 273.1140.

Representative synthetic procedure for 6-hydroxy indoles (**3a-3x**) and (**5a-5d**): Primary amine (0.24 mmol, 1.2 equiv) was added to **1** (0.2 mmol, 1 equiv) dissolved in toluene (1.5 mL) along with 4 A° molecular sieves at rt. The reaction mixture was stirred at ambient temperature. After the completion of starting material (monitored by TLC), the reaction mixture was purified by column chromatography (EtOAc/n-Hexane) using silica-gel as stationary phase to get the pure 6-hydroxy indoles **3** or **5**.

1-Phenyl-1*H*-indol-6-ol (**3a**):[14a] 28 mg, 66% yield; R_f = 0.24 (30:70 = EtOAc/n-Hexane); Green colored solid; mp: 96-99 °C; **FT-IR (neat)**: 3340, 2914, 2848, 2360, 2334, 1614, 1596, 1506, 1335, 1215, 1096, 930, 807 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.57-7.42 (m, 5H), 7.37-7.30 (m, 1H), 7.22 (d, *J* = 3.2 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.73 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.61 (d, *J* = 3.1 Hz, 1H), 4.96 (s, 1H); **^{13}C NMR (100 MHz, CH_3Cl_3)**: δ, 152.1, 139.8, 136.6, 129.6, 127.0, 126.4, 124.2, 123.6, 121.7, 110.3, 103.5, 96.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{14}H_{12}NO$: 210.0913; found: 210.0920.

1-(4-Methoxyphenyl)-1*H*-indol-6-ol (**3b**): 37 mg, 78% yield; R_f = 0.32 (30:70 = EtOAc/n-Hexane); Brown colored semi solid; **FT-IR (neat)**: 3388, 2924, 2848, 2358, 1620, 1412, 1248, 1029, 931, 829 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.53 (d, *J* = 8.4 Hz, 1H), 7.45-7.37 (m, 2H), 7.19 (d, *J* = 3.2 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 2.1 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 158.2, 152.1, 137.2, 132.8, 127.4, 125.9, 123.3, 121.7, 114.7, 110.1, 102.9, 96.2, 55.6; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{15}H_{13}NO_2$: 239.0946; found: 239.0928

1-(4-(Dimethylamino)phenyl)-1*H*-indol-6-ol (**3c**): 36 mg, 71% yield; R_f = 0.39 (30:70 = EtOAc/n-Hexane); Black colored solid; mp: 130-132 °C; **FT-IR (neat)**: 3342, 2922, 2810, 2353, 2322, 1614, 1524, 1477, 146, 1352, 1205, 1095, 937, 813 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.53 (d, *J* = 8.5 Hz, 1H), 7.36-7.30 (m, 2H), 7.19 (d, *J* = 3.2 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.86-6.81 (m, 2H), 6.75 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.59 (d, *J* = 3.2 Hz, 1H), 3.02 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 152.1, 149.4, 137.3, 129.4, 127.6, 125.6, 123.2, 121.5, 113.3, 110.0, 102.4, 96.4, 40.9; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{16}H_{16}N_2O$: 252.1263; found: 252.1259.

1-(4-Bromophenyl)-1*H*-indol-6-ol (**3d**): 47 mg, 72% yield; R_f = 0.25 (10:90 = EtOAc/n-Hexane); Light brown colored sticky solid; **FT-IR (neat)**: 3354, 2921, 2830, 1621, 1588, 1490, 1454, 1338, 1210, 1196, 1071, 1009, 931, 825, 715 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.65 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 3.3 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.64 (dd, *J* = 3.3, 0.8 Hz, 1H), 4.75 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 152.4, 138.9, 136.5, 132.8, 126.8, 125.7, 123.7, 121.9, 119.7, 110.5, 104.1, 96.3; **GC HR-MS (ESI, *m/z*)**: $[M+K]^+$ calculated for $C_{14}H_{10}BrNOK$: 325.9577; found: 325.9602.

1-(Pyridin-2-yl)-1*H*-indol-6-ol (**3e**): 33 mg, 78% yield; R_f = 0.35 (30:70 = EtOAc/n-Hexane); Yellow colored solid; mp: 120-124 °C; **FT-IR (neat)**: 3437, 2954, 2920, 2357, 2336, 1624, 1504, 1342, 1209, 931, 756 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$):** δ, 8.56 (d, *J* = 4.7 Hz, 1H), 7.83 (s, 1H), 7.81 (d, *J* = 8.1

Hz, 1H), 7.59 (d, *J* = 3.4 Hz, 1H), 7.47 (dd, *J* = 23.6, 8.3 Hz, 2H), 7.22-7.07 (m, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 3.3 Hz, 1H), 5.42 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 152.7, 148.8, 138.5, 135.9, 124.7, 121.6, 119.9, 114.2, 111.0, 105.7, 99.7; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{13}H_{10}N_2O$: 210.0793; found: 210.0791.

1-(9*H*-fluoren-2-yl)-1*H*-indol-6-ol (**3f**): 49 mg, 82% yield; R_f = 0.54 (20:80 = EtOAc/n-Hexane); Dark brown colored semi solid; **FT-IR (neat)**: 3385, 3051, 2924, 2852, 2304, 1705, 1616, 1462, 1263, 1211, 943, 738 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.89 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.09 (s, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.65 (d, *J* = 3.1 Hz, 1H), 4.87 (s, 1H), 3.99 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 152.2, 144.7, 143.3, 140.9, 140.2, 138.5, 136.9, 127.3, 127.0, 126.9, 125.1, 123.7, 123.1, 121.8, 121.1, 120.6, 120.0, 110.3, 103.4, 96.6, 37.0; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{21}H_{16}NO$: 298.1226; found: 298.1200.

1-Cyclopentyl-1*H*-indol-6-ol (**3g**): 33 mg, 83% yield; R_f = 0.43 (20:80 = EtOAc/n-Hexane); Dark brown colored semi solid; **FT-IR (neat)**: 3360, 2958, 2870, 1622, 1477, 1462, 1365, 1211, 1197, 947, 894, 628 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.44 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.83 (d, *J* = 1.5 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 4.75-4.47 (m, 1H), 2.15 (d, *J* = 7.2 Hz, 2H), 1.88 (dt, *J* = 13.5, 7.5 Hz, 4H), 1.80-1.63 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 151.3, 137.0, 123.6, 123.2, 121.5, 109.4, 100.9, 95.9, 57.0, 32.4, 24.1; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{13}H_{16}NO$: 202.1226; found: 202.1223.

1-Cyclohexyl-1*H*-indol-6-ol (**3h**): 34 mg, 80% yield; R_f = 0.42 (20:80 = EtOAc/n-Hexane); Black colored solid; mp: 99-102 ^oC; **FT-IR (neat)**: 3361, 2931, 2854, 2665, 1622, 1581, 1458, 1369, 1259, 1207, 945, 802, 738, 705 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.44 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.82 (d, *J* = 1.8 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.41 (d, *J* = 3.1 Hz, 1H), 4.05 (tt, *J* = 11.8, 3.6 Hz, 1H), 2.10 (d, *J* = 11.3 Hz, 2H), 1.92 (d, *J* = 13.3 Hz, 2H), 1.67 (ddd, *J* = 24.6, 12.5, 3.2 Hz, 2H), 1.54-1.36 (m, 2H), 1.35-1.18 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 151.3, 136.4, 123.2, 123.0, 121.5, 109.3, 101.0, 95.5, 55.2, 33.3, 29.7, 26.0, 25.7; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{14}H_{18}NO$: 216.1383; found: 216.1388.

1-Cycloheptyl-1*H*-indol-6-ol (**3i**): 40 mg, 87% yield; R_f = 0.57 (30:70 = EtOAc/n-Hexane); Brown colored semi solid; **FT-IR (neat)**: 3365, 2926, 2858, 1622, 1450, 1383, 1213, 1178, 946, 806, 767 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.43 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.80 (d, *J* = 1.7 Hz,

1H), 6.63 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.40 (d, *J* = 3.1 Hz, 1H), 4.83 (s, 1H), 4.24 (ddd, *J* = 14.3, 10.2, 3.9 Hz, 1H), 2.15-2.06 (m, 2H), 1.92 (ddd, *J* = 10.1, 8.4, 3.2 Hz, 2H), 1.81 (ddd, *J* = 18.8, 13.0, 9.4 Hz, 2H), 1.73 – 1.51 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.3, 136.2, 123.6, 122.9, 121.5, 109.2, 101.0, 95.5, 57.5, 35.3, 27.7, 25.1; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{15}H_{19}NO$: 229.1467; found: 229.1446.

1-Benzyl-1*H*-indol-6-ol (**3j**):[14b] 37 mg, 80% yield; R_f = 0.68 (30:70 = EtOAc/n-Hexane); White colored solid; mp: 93-95 ^oC; **FT-IR (neat)**: 3367, 2921, 2857, 1622, 1487, 1472, 1362, 12361, 1175, 1041, 946, 801 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.46 (d, *J* = 8.4 Hz, 1H), 7.31-7.21 (m, 3H), 7.08 (d, *J* = 6.7 Hz, 2H), 7.00 (d, *J* = 3.2 Hz, 1H), 6.68 (s, 1H), 6.65 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.46 (d, *J* = 2.8 Hz, 1H), 5.21 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.7, 137.4, 137.2, 128.8, 127.6, 127.4, 126.7, 123.2, 121.6, 109.6, 101.7, 95.6, 50.1; **LR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{15}H_{14}NO$: 224.1; found: 224.0.

1-Benzhydryl-1*H*-indol-6-ol (**3k**): 45 mg, 75% yield; R_f = 0.64 (30:70 = EtOAc/n-Hexane); Dark brown colored solid; mp: 118-120 ^oC; **FT-IR (neat)**: 3387, 3054, 3030, 2424, 1957, 1622, 1442, 1426, 1350, 1207, 947, 808, 746 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.46 (d, *J* = 9.0 Hz, 1H), 7.36-7.27 (m, 6H), 7.13-7.05 (m, 4H), 6.70 (d, *J* = 3.3 Hz, 1H), 6.67 (s, 1H), 6.67-6.63 (m, 2H), 6.40 (d, *J* = 3.2 Hz, 1H), 4.60 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 151.5, 139.7, 137.4, 128.7, 128.4, 127.9, 126.1, 121.6, 109.8, 101.4, 96.3, 63.7; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{21}H_{18}NO$: 300.1383; found: 300.1392.

1-(1-Phenylethyl)-1*H*-indol-6-ol (**3l** or **5a**): 36 mg, 76% yield; R_f = 0.43 (30:70 = EtOAc/n-Hexane); Yellow colored thick liquid; **FT-IR (neat)**: 3367, 2980, 2370, 1955, 1872, 1620, 1496, 1458, 1361, 1193, 1097, 939, 808 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.50 (d, *J* = 9.0 Hz, 1H), 7.34-7.29 (m, 2H), 7.29-7.24 (m, 1H), 7.23 (d, *J* = 3.3 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.71-6.66 (m, 2H), 6.54 (d, *J* = 3.3 Hz, 1H), 5.53 (q, *J* = 7.1 Hz, 1H), 1.91 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 151.5, 142.7, 137.0, 128.7, 127.4, 125.9, 124.0, 123.3, 121.5, 109.7, 101.5, 96.2, 54.9, 21.7; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{16}H_{16}NO$: 238.1226; found: 238.1220; $[\alpha]_D^{24.7}$ = +87.14 (c = 1.3, $CHCl_3$, >99% ee).

The enantiomeric ratio of **5a** was determined by HPLC analysis using a Daicel Chiralpak OZ-3 column (Hexane/ 2-propanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), t_R = 4.6 min (minor), t_R = 6.2 min (major).

1-(2-Bromoethyl)-1*H*-indol-6-ol (**3m**): Amines were used in the form of ammonium salt along with same reaction conditions. 2-3 Drops of aq$NaHCO_3$ was used; 27 mg, 58% yield; R_f = 0.5 (30:70 = EtOAc/n-Hexane); Pink colored semi solid; **FT-IR (neat)**: 3385, 2458, 2922, 1622, 1485, 1361, 1201, 1143, 945, 817 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.49 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.80 (s, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 3.0 Hz, 1H), 4.78 (s, 1H), 4.45 (t, *J* = 7.0 Hz, 2H), 3.64 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 152.0, 136.6, 127.0, 123.2, 121.9, 109.8, 102.0, 95.0, 48.0, 29.6; **HR-MS (GC, *m/z*)**: $[M]^+$ calculated for $C_{10}H_{10}BrNO$: 238.9946; found: 238.9938.

1-(2-(Cyclohex-2-en-1-yl)ethyl)-1*H*-indol-6-ol (**3n**): 34 mg, 70% yield; R_f = 0.75 (30:70 = EtOAc/n-Hexane); Dark colored semi solid; **FT-IR (neat)**: 3363, 3043, 2926, 2858, 2663, 1624, 1510, 1405, 1361, 1172, 1172, 1043, 804 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.43 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 3.1 Hz, 1H), 6.77 (d, *J* = 1.4 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.38 (d, *J* = 3.0 Hz, 1H), 5.38 (s, 1H), 4.13-4.01 (m, 2H), 2.43-2.28 (m, 2H), 2.00-1.87 (m, 4H), 1.66-1.57 (m, 2H), 1.56-1.48 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.5, 136.8, 134.4, 126.9, 123.8, 123.1, 121.5, 109.3, 100.8, 95.3, 45.4, 38.3, 28.5, 25.3, 22.9, 22.3; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{16}H_{20}NO$: 242.1539; found: 242.1545.

1-(2-Morpholinoethyl)-1*H*-indol-6-ol (**3o**):[14c] 20 mg, 40% yield; R_f = 0.15 (60:40 = EtOAc/n-Hexane); Yellow colored semi solid; **FT-IR (neat)**: 3317, 2956, 2924, 1622, 1577, 1462, 1367, 1267, 1205, 1114, 1008, 810 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.41 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 3.2 Hz, 1H), 6.77 (d, *J* = 1.7 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.39 (d, *J* = 2.9 Hz, 1H), 5.50 (s, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 3.85-3.65 (m, 4H), 2.84-2.62 (m, 2H), 2.61-2.47 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 152.2, 136.8, 126.8, 122.8, 121.7, 109.8, 101.6, 95.2, 66.3, 57.6, 53.5, 43.3; **LR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{14}H_{19}N_2O_2$: 247.1; found: 247.0.

1-(2-(1*H*-indol-3-yl)ethyl)-1*H*-indol-6-ol (**3p**): 39 mg, 70% yield; R_f = 0.39 (30:70 = EtOAc/n-Hexane); Pink colored semi solid; **FT-IR (neat)**: 3404, 3324, 2923, 2848, 2250, 2360, 1622, 1511, 1370, 1231, 1025, 761 cm^{-1}; **^{1}H NMR (400 MHz, DMSO)**: δ, 10.81 (s, 1H), 8.96 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 16.5, 8.2 Hz, 2H), 7.06 (dd, *J* = 15.9, 5.3 Hz, 3H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.80 (s, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 6.22 (d, *J* = 2.6 Hz, 1H), 4.26 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR (100 MHz, DMSO)**: δ, 153.5, 137.1, 136.6, 127.5, 127.2, 123.5, 121.9, 121.5, 121.3, 118.9, 118.7, 111.9, 111.4, 109.9, 100.8, 95.3, 46.7, 26.1; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{18}H_{17}N_2O$: 277.1335; found: 277.1316.

1-Allyl-1*H*-indol-6-ol (**3q**):[14d] 25 mg, 73% yield; R_f = 0.54 (30:70 = EtOAc/n-Hexane); Dark brown colored solid; **FT-IR (neat)**: 3360, 2920, 2820, 1624, 1487, 1413, 1348, 1267, 1184, 943, 804, 715 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.45 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 2.9 Hz, 1H), 6.75 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 2.9 Hz, 1H), 5.95 (ddd, *J* = 21.6, 10.4, 5.3 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 4.82 (s, 1H), 4.61 (d, *J* = 5.1 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 151.6, 137.0, 133.3, 127.0, 123.2, 121.6, 117.3, 109.5, 101.4, 95.6, 48.9; **LR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{11}H_{12}NO$: 174.1; found: 174.0.

Ethyl 2-(6-hydroxy-1*H*-indol-1-yl)acetate (**3r**): Amines was used in the form of ammonium salt, along with same reaction conditions. 2-3 Drops of aq $NaHCO_3$ was used; 21 mg, 49% yield; R_f = 0.28 (30:70 = EtOAc/n-Hexane); Maroon colored solid; mp: 70-73 °C; **FT-IR (neat)**: 3417, 2984, 2935, 1731, 1622, 1584, 1489, 1470, 1344, 1322, 1271, 1022, 947, 819 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.42 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 3.2 Hz, 1H), 6.70-6.62 (m, 2H), 6.46 (d, *J* = 3.1 Hz, 1H), 5.85 (s, 1H), 4.69 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 169.0, 152.3, 137.5, 127.5, 122.9, 121.7, 110.0, 102.5, 95.1, 61.8, 47.9, 14.1; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{12}H_{14}NO_3$: 220.0968; found: 220.0980.

1*H*-indol-6-ol (**3s**):[14e] 24 mg, 92% yield; R_f = 0.28 (30:70 = EtOAc/n-Hexane); Light green colored solid; mp: 86-89 °C; **FT-IR (neat)**: 3388, 2954, 2920, 2357, 2336, 1624, 1504, 1456, 1209, 1047, 812, 715 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 8.01 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.11 (s, 1H), 6.87 (s, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.50 (s, 1H), 4.78 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 151.9, 136.6, 123.2, 122.4, 121.3, 109.9, 102.5, 96.8; **LR-MS (ESI, *m/z*)**: $[M]^+$ calculated for C_8H_7NO: 133.1; found: 133.1.

1-Benzyl-2-methyl-1*H*-indol-6-ol (**3t**): 42 mg, 90% yield; R_f = 0.64 (30:70 = EtOAc/n-Hexane); Brown colored solid; mp: 90-92 °C; **FT-IR (neat)**: 3377, 2924, 1620, 1481, 1458, 1394, 1352, 1209, 1184, 946, 813, 727 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.40 (d, *J* = 8.6 Hz, 1H), 7.29 (m, *J* = 7.2 Hz, 3H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 6.6 Hz, 2H), 6.27 (s, 1H), 5.22 (s, 2H), 2.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.1, 138.0, 137.8, 135.8, 128.8, 127.3, 126.0, 122.6, 120.3, 109.2, 100.2, 95.7, 46.5, 12.7; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{16}H_{15}NO$: 237.1154; found: 237.1149.

1-Benzyl-2-ethyl-1*H*-indol-6-ol (**3u**): 46 mg, 92% yield; R_f = 0.36 (20:80 = EtOAc/n-Hexane); Dark green colored semi solid; **FT-IR (neat)**: 3367, 2971, 2936, 2360, 2334, 1620, 1455, 1316, 1200, 1105, 820. cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.45-7.35 (m, 1H), 7.30-7.17 (m, 3H), 6.95 (d, *J* = 6.8 Hz,

2H), 6.65-6.57 (m, 2H), 6.26 (s, 1H), 5.20 (s, 2H), 2.64 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.1, 142.0, 138.1, 137.83, 128.8, 127.2, 126.0, 122.6, 120.4, 109.2, 98.3, 95.6, 46.4, 19.9, 12.6; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{17}H_{18}NO$: 252.1383; found: 252.1382.

1-Benzyl-3-methyl-1*H*-indol-6-ol (**3v**): 38 mg, 78% yield; R_f = 0.54 (20:80 = EtOAc/n-Hexane); White colored solid; mp: 127-130 ^oC; **FT-IR (neat)**: 3332, 2922, 2856, 1620, 1598, 1496, 1456, 1381, 1257, 1205, 1120, 758, 696 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.48-7.39 (m, 1H), 7.35-7.25 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.80 (s, 1H), 6.74-6.60 (m, 2H), 5.18 (s, 2H), 4.75 (s, 1H), 2.33 (d, *J* = 0.6 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 151.8, 137.8, 137.5, 128.7, 127.5, 126.8, 124.9, 123.7, 119.7, 110.9, 108.8, 95.5, 49.8, 9.7; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{16}H_{16}NO$: 238.1226; found: 238.1249.

Ethyl 2-(6-hydroxy-2-methyl-1*H*-indol-1-yl)acetate (**3w**): Amines was used in the form of ammonium salt along with same reaction conditions. 2-3 Drops of aq $NaHCO_3$ was used; 22 mg, 47% yield; R_f = 0.44 (30:70 = EtOAc/n-Hexane); Dark green colored solid; mp: 101-103 ^oC; **FT-IR (neat)**: 3391, 2931, 1731, 1668, 1622, 1515, 1487, 1394, 1200, 1095, 947, 863, 823, 706 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.31 (d, *J* = 9.0 Hz, 1H), 6.63-6.53 (m, 2H), 6.19 (s, 1H), 5.10 (s, 1H), 4.66 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 169.0, 151.4, 138.1, 135.4, 130.6, 122.5, 120.5, 109.5, 100.7, 95.0, 61.7, 44.9, 14.1, 12.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{13}H_{16}NO_3$: 234.1125; found: 234.1115.

3-Methyl-1-phenyl-1*H*-indol-6-ol (**3x**): 33 mg, 74% yield; R_f = 0.57 (30:70 = EtOAc/n-Hexane); Dark yellow colored semi solid; **FT-IR (neat)**: 3373, 3332, 3045, 2922, 2856, 1620, 1598, 1496, 1450, 1381, 1257, 1205, 1120, 758 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.49 (m, *J* = 8.2 Hz, 5H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.05 (s, 2H), 6.76 (dd, *J* = 8.5, 1.6 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 152.4, 140.0, 136.8, 129.6, 125.9, 124.48, 124.4, 123.8, 119.9, 112.9, 109.6, 96.4, 9.6; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{15}H_{14}NO$: 224.1070; found: 224.1081.

Representative synthetic procedure for the synthesis of 6-hydroxy indoles (**4a-4d**)**:** Primary amine (0.24 mmol, 1.2 equiv) was added to **1a** (0.2 mmol, 1 equiv) dissolved in dichloromethane (1.5 mL) at rt. To this reaction mixture, Re_2O_7 (5 mol %) was added and the reaction mixture was stirred at ambient temperature. After completion of the starting material (monitored by TLC), the solvent was removed

under reduced pressure. The residue was purified by column chromatography (EtOAc/n-Hexane) on silica-gel to get the pure 6-hydroxyindoles **4a-4d**.

1-Tosyl-1*H*-indol-6-ol (**4a**):[14f] 37 mg, 65% yield; R_f = 0.46 (30:70 = EtOAc/n-Hexane); White colored solid; mp: 116-119 °C; **FT-IR (neat)**: 3394, 2922, 2854, 2854, 1618, 1485, 1442, 1361, 1300, 1197, 1166, 1118, 815, 675 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.71 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.42 (d, *J* = 3.6 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.78 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.55 (d, *J* = 3.4 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 153.7, 144.9, 135.8, 129.9, 126.8, 125.1, 124.6, 122.1, 112.8, 109.1, 100.2, 21.5; **LR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{15}H_{13}NO_3S$: 287.1; found: 287.9.

1-((4-Nitrophenyl)sulfonyl)-1*H*-indol-6-ol (**4b**): 41 mg, 66% yield; R_f = 0.43 (30:70 = EtOAc/n-Hexane); Yellow colored solid; mp: 80-82 °C; **FT-IR (neat)**: 3361, 2954, 2922, 2360, 2230, 1614, 1531, 1373, 1197, 1116, 1004, 854, 740 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 8.37-8.18 (m, 2H), 8.09-7.88 (m, 2H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 3.7 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.71-6.55 (m, 1H), 5.48 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 154.2, 150.6, 143.3, 135.8, 128.0, 124.8, 124.7, 124.5, 122.5, 113.5, 110.7, 100.2; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{14}H_{11}N_2O_5S$: 319.0383; found: 319.0382.

1-(4-Nitrophenyl)-1*H*-indol-6-ol (**4c**): 35 mg, 68% yield; R_f = 0.6 (30:70 = EtOAc/n-Hexane); Brown colored solid; mp: 155-158 °C; **FT-IR (neat)**: 3994, 3447, 2922, 2852, 2447, 2358, 1595, 1508, 1452, 1332, 1203, 1107, 929, 875, 750 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 8.41 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 1.3 Hz, 1H), 7.15 (s, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 3.1 Hz, 1H), 4.87 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 152.9, 145.4, 145.1, 136.1, 126.2, 125.5, 124.3, 123.2, 122.3, 111.3, 106.2, 96.8; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{14}H_{10}N_2O_3$: 254.0691; found: 254.0669.

4-(6-Hydroxy-1*H*-indol-1-yl)benzonitrile (**4d**): 22 mg, 65% yield; R_f = 0.43 (30:70 = EtOAc/n-Hexane); Yellow colored solid; mp: 131-133 °C; **FT-IR (neat)**: 3394, 2922, 2852, 2350, 2229, 1602, 1512, 1462, 1342, 1205, 10095, 929, 829 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.85-7.73 (m, 2H), 7.67-7.62 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.69 (dd, *J* = 3.4, 0.6 Hz, 1H), 5.09 (s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 152.9, 143.7, 136.1, 133.8, 126.1, 124.2, 123.7, 122.2, 118.5, 111.2, 109.2, 105.8, 96.6; **GC HR-MS (ESI, *m/z*)**: $[M]^+$ calculated for $C_{15}H_{10}N_2O$: 234.0793; found: 234.0787.

(R)-1-(1-(Naphthalen-1-yl)ethyl)-1*H*-indol-6-ol (**5b**): 31 mg, 54% yield; R_f = 0.29 (20:80 = EtOAc/n-Hexane); Amber coloured semi solid; **FT-IR (neat)**: 3390, 2978, 2926, 1705, 1622, 1508, 1460, 1207, 1099, 1035, 707 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 8.05-7.97 (m, 1H), 7.92 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.56-7.45 (m, 3H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 11.1, 5.2 Hz, 2H), 6.68 (d, *J* = 6.5 Hz, 2H), 6.48 (d, *J* = 3.1 Hz, 1H), 6.29 (q, *J* = 6.9 Hz, 1H), 4.66 (s, 1H), 2.02 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 151.6, 137.7, 136.8, 133.9, 130.7, 129.1, 128.4, 126.7, 125.8, 125.6, 124.3, 123.4, 123.1, 122.4, 121.6, 109.7, 101.4, 95.8, 51.4, 20.9; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{20}H_{18}NO$: 288.1383; found: 288.1360; $[\alpha]_D^{24.4}$ = +3.28 (c = 0.25, $CHCl_3$, >99% ee).

The enantiomeric ratio was determined by HPLC analysis using a Daicel Chiralpak IC-3 column (Hexane/ 2-propanol = 96:04, flow rate 1.0 mL/min, λ = 254 nm), t_R = 30.5 min (minor), t_R = 38.0 min (major).

2-Methyl-1-(1-phenylethyl)-1*H*-indol-6-ol (**5c**): 40 mg, 79% yield; R_f = 0.29 (30:70 = EtOAc/n-Hexane); Yellow colored semi solid; **FT-IR (neat)**: 3380, 2914, 2350, 2338, 1616, 1467, 1394, 1189, 1088, 801, 695 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.31 (dd, *J* = 16.9, 8.0 Hz, 3H), 7.24 (dd, *J* = 6.2, 3.5 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.56 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.45 (d, *J* = 1.6 Hz, 1H), 6.20 (s, 1H), 5.65 (q, *J* = 7.1 Hz, 1H), 2.33 (s, 3H), 1.90 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 150.4, 141.3, 136.6, 135.8, 128.6, 127.2, 126.3, 123.0, 120.2, 108.9, 100.7, 97.4, 52.4, 18.4, 13.9; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{31}H_{38}N_2O$: 455.3057; found: 455.3077; $[\alpha]_D^{24.1}$ = +18.25 (c = 0.2, $CHCl_3$, >99% ee).

The enantiomeric ratio was determined by HPLC analysis using a Daicel Chiralpak OZ-3 column (Hexane/ 2-propanol = 96:04, flow rate 0.5 mL/min, λ = 254 nm), t_R = 33.6 min (minor), t_R = 35.8 min (major).

Methyl (R)-2-(6-hydroxy-1*H*-indol-1-yl)propanoate (**5d**): Amines was used in the form of ammonium salt under the same reaction conditions. 2-3 Drops of aq $NaHCO_3$ was used; 18 mg, 41% yield; R_f = 0.28 (30:70 = EtOAc/n-Hexane); Yellow coloured liquid; **FT-IR (neat)**: 3314, 2989, 2852, 1741, 1624, 1460 1355, 1265 1168, 939, 738 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.43 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 1H), 6.66 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.47 (d, *J* = 3.2 Hz, 1H), 5.08 – 4.93 (m, 1H), 3.68 (s, 3H), 1.78 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 171.9, 152.0, 137.0, 124.1, 123.0, 121.7, 109.9, 102.5, 95.3, 53.6, 52.6, 17.4; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{12}H_{14}NO_3$: 220.0968; found: 220.0963. $[\alpha]_D^{24.4}$ = +47.95 (c = 0.2, $CHCl_3$).

(*R*)-1-(1-Hydroxybutan-2-yl)-1*H*-indol-6-ol (**5e**): 31 mg, 75% yield; R_f = 0.14 (30:70 = EtOAc/n-Hexane); White colored solid; mp:81-84 ^oC; **FT-IR (neat)**: 3368, 2965, 2926, 1627, 1465, 1312, 1207, 1047, 937, 864, 711 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.46 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.65 (s, 1H), 6.49 (d, *J* = 3.0 Hz, 1H), 3.91 – 3.80 (m, 1H), 3.68 (m, *J* = 11.5, 8.3 Hz, 1H), 3.54 (dd, *J* = 11.6, 4.0 Hz, 1H), 1.83-1.68 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.4, 138.2, 122.9, 122.7, 121.5, 109.9, 102.2, 96.0, 65.3, 59.6, 24.3, 10.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{12}H_{16}NO_2$: 206.1176; found: 206.1161. $[\alpha]_D^{26.4}$ = +22.29 (c = 0.69, $CHCl_3$).

(*S*)-1-(1-Hydroxy-3-phenylpropan-2-yl)-1*H*-indol-6-ol (**5f**): 32 mg, 60% yield; R_f = 0.17 (30:70 = EtOAc/n-Hexane); Brown colored semi solid; **FT-IR (neat)**: 3389, 3029, 2924, 2855, 1621, 1464, 1372, 1317, 1197, 1032, 939, 804 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.44 (d, *J* = 8.4 Hz, 1H), 7.25-7.16 (m, 3H), 7.10 (d, *J* = 3.0 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.72 (s, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 16.6 Hz, 1H), 5.20 (s, 1H), 4.49 (dq, *J* = 13.5, 6.7 Hz, 1H), 3.94-3.80 (m, 2H), 3.37 – 3.05 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.7, 137.5, 128.9, 128.6, 126.7, 123.8, 122.938, 121.6, 109.8, 102.2, 95.6, 64.1, 59.5, 37.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{17}H_{18}NO_2$: 268.1332; found: 268.1313. $[\alpha]_D^{23.8}$ = -9.06 (c = 0.395, $CHCl_3$).

(*S*)-1-(1-Hydroxy-4-(methylthio)butan-2-yl)-1*H*-indol-6-ol (**5g**): 19 mg, 38% yield; R_f = 0.14 (30:70 = EtOAc/n-Hexane); Yellow colored semisolid; **FT-IR (neat)**: 3834, 3417, 2922, 2853, 1646, 1621, 1487, 1456, 1373, 1313, 1197, 1044, 938, 804 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.47 (d, *J* = 8.4 Hz, 1H), 7.08 (s, 1H), 6.86 (s, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.8 Hz, 1H), 5.20 (s, 1H), 4.53 (m, *J* = 15.7, 11.0 Hz, 1H), 4.04-3.83 (m, 2H), 2.44-2.34 (m, 1H), 2.33-2.22 (m, 1H), 2.21-2.08 (m, 2H), 2.05 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.8, 137.8, 123.2, 122.9, 121.7, 110.0, 102.8, 95.7, 65.3, 56.7, 30.5, 30.4, 15.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{13}H_{18}NO_2S$: 252.1053; found: 252.1053. $[\alpha]_D^{23.1}$ = +3.92 (c = 0.255, $CHCl_3$).

(S)-1-(1-Hydroxy-3-(1*H*-indol-3-yl)propan-2-yl)-1*H*-indol-6-ol (**5h**): 33 mg, 55% yield; R_f = 0.28 (40:60 = EtOAc/n-Hexane); Amber colored semi solid; **FT-IR (neat)**: 3429, 2914, 2843, 1634, 1456, 1366, 1209, 1101, 1045, 1024, 992, 820 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-D_6)**: δ, 10.71 (s, 1H), 8.89 (d, *J* = 2.9 Hz, 1H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.33 (s, 1H), 7.31-7.25 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 6.9 Hz, 1H), 6.82 (s, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.56-6.47 (m, 1H), 6.28 (s, 1H), 4.95 (d, *J* = 4.2 Hz, 1H), 4.58 (s, 1H), 3.74 (s, 2H), 3.38 (m, 1H), 3.21 (dd, *J* = 11.7, 9.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-D_6)**: δ, 153.3, 137.8, 136.4, 127.7, 124.5, 123.5, 121.7, 121.3, 121.0, 118.8, 118.5, 111.8,

111.2, 109.8, 101.0, 95.6, 63.7, 58.5, 27.0; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{19}H_{19}N_2O_2$: 307.1441; found: 307.1439. $[\alpha]_D^{23.1}$ = -9.63 (c = 1.59, AcCN).

(*S*)-1-(1,2,3,4-Tetrahydronaphthalen-1-yl)-1*H*-indol-6-ol (**5i**): 30 mg, 58% yield; R_f = 0.46 (30:70 = EtOAc/n-Hexane); Dark brown colored semi solid; **FT-IR (neat)**: 3428, 2931, 2866, 1622, 1505, 1487, 1353, 1320, 1203, 949, 741 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.50 (d, *J* = 8.4 Hz, 1H), 7.27-7.20 (m, 2H), 7.13-7.06 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.82-6.77 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 3.1 Hz, 1H), 5.55 (t, *J* = 6.6 Hz, 1H), 4.78 (s, 1H), 3.02 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.91 (dt, *J* = 16.9, 5.9 Hz, 1H), 2.31-2.13 (m, 2H), 2.01-1.79 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 151.4, 137.8, 136.9, 135.3, 129.2, 128.8, 127.6, 126.4, 126.3, 123.3, 121.7, 109.5, 101.1, 95.9, 54.9, 30.3, 29.3, 20.8; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{18}H_{18}NO$: 264.1383; found: 264.1376. $[\alpha]_D^{23.9}$ = -42.05 (c = 0.85, $CHCl_3$).

Representative synthetic procedure for the synthesis of 6-aminoindoles (**6a-6e**): Primary amine (0. 44 mmol, 2.2 equiv) was added to **1** (0.2 mmol, 1 equiv) dissolved in dichloromethane (1.5 mL) at rt. To this reaction mixture, Re_2O_7 (5 mol %) was added, and the reaction mixture was stirred at ambient temperature. After completion of the starting material (monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by column chromatography (EtOAc/n-Hexane) on silica-gel to get the pure 6-aminoindoles **6a-6e**.

N,1-Dibenzyl-2-phenyl-1*H*-indol-6-amine (**6a**): 47 mg, 60% yield; R_f = 0.64 (30:70 = EtOAc/n-Hexane); Green colored semi solid; **FT-IR (neat)**: 3414, 2920, 2852, 1624, 1500, 1460, 1354, 1029, 808, 732 cm^{-1}; **^{1}H NMR (700 MHz, $CDCl_3$)**: δ, 7.48 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 13.9, 7.1 Hz, 4H), 7.31-7.26 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.55 (s, 1H), 6.39 (s, 1H), 5.26 (s, 2H), 4.29 (s, 2H); **^{13}C NMR (175 MHz, $CDCl_3$)**: δ, 144.6, 139.7, 138.3, 137.50, 133.1, 130.3, 128.9, 128.7, 128.6, 128.5, 127.7, 127.4, 127.1, 127.0, 126.1, 121.2, 120.9, 109.9, 102.3, 93.2, 49.1, 47.8, 29.7; **GC HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{28}H_{24}N_2$: 389.2012; found: 389.1997.

N,1,2-Triphenyl-1*H*-indol-6-amine (**6b**): 59 mg, 82% yield; R_f = 0.64 (30:70 = EtOAc/n-Hexane); White colored solid; mp: 142-145 ^oC; **FT-IR (neat)**: 3394, 2358, 2330, 1597, 1496, 1307, 1178, 1078, 806, 754 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.61 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.23 (dd, *J* = 18.5, 6.5 Hz, 9H), 7.09-7.01 (m, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.78 (s, 1H), 5.69 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 145.0, 140.3, 140.0, 138.6,

138.1, 132.6, 129.3, 129.3, 128.7, 128.2, 128.0, 127.2, 127.1, 124.1, 121.2, 119.7, 116.0, 115.5, 103.8, 101.8; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{26}H_{21}N_2$: 361.1699; found: 361.1714.

N,1-Bis(2-(cyclohex-2-en-1-yl)ethyl)-2-(4-methoxyphenyl)-1*H*-indol-6-amine (**6c**): 64 mg, 70% yield; R_f = 0.64 (30:70 = EtOAc/n-Hexane); Black colored solid; mp: 70-72 ^oC; **FT-IR (neat)**: 3398, 2926, 2835, 2360, 2333, 1742, 1622, 1546, 1502, 1475, 1357, 1280, 1246, 1176, 1035, 804 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.47-7.35 (m, 3H), 7.08-6.74 (m, 2H), 6.66-6.47 (m, 2H), 6.35 (s, 1H), 5.60 (s, 1H), 5.36 (s, 1H), 4.23-4.07 (m, 2H), 3.90 (s, 3H), 3.29 (t, *J* = 6.8 Hz, 2H), 2.36 (t, *J* = 6.6 Hz, 2H), 2.34-2.30 (m, 2H), 2.12-2.06 (m, 2H), 2.02 (s, 2H), 1.95 (d, *J* = 3.4 Hz, 2H), 1.84 (s, 2H), 1.73 – 1.65 (m, 2H), 1.65-1.59 (m, 2H), 1.59-1.50 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 159.1, 144.5, 138.8, 138.7, 135.2, 134.7, 130.5, 126.2, 123.5, 123.2, 120.9, 120.8, 113.8, 109.8, 101.4, 92.7, 55.4, 43.0, 42.6, 38.0, 37.7, 28.4, 28.0, 25.3, 25.2, 22.9, 22.8, 22.5, 22.2; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{31}H_{39}N_2O$: 455.3057; found: 455.3075.

N,1-Dibenzyl-2-(4-methoxyphenyl)-1*H*-indol-6-amine (**6d**): 48 mg, 57% yield; R_f = 0.68 (30:70 = EtOAc/n-Hexane); White colored solid; mp: 152-155 ^oC; **FT-IR (neat)**: 3464, 3026, 2922, 2848, 1614, 1573, 1454, 1355, 1247, 1176, 1028, 835, 731 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.44 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 7.6, 5.1 Hz, 6H), 7.25 (dt, *J* = 8.4, 5.5 Hz, 4H), 7.03 (d, *J* = 6.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), 6.37 (s, 1H), 5.21 (s, 2H), 4.26 (s, 2H), 3.81 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 159.2, 144.4, 139.7, 139.5, 139.4, 138.5, 130.3, 128.7, 128.6, 127.7, 127.1, 127.0, 126.1, 125.7, 121.0, 114.0, 109.8, 101.6, 93.3, 55.3, 49.2, 47.7; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{29}H_{27}N_2O$: 419.2118; found: 419.2116.

2-(4-Methoxyphenyl)-N,1-bis((R)-1-phenylethyl)-1*H*-indol-6-amine (**6e**): 80 mg, 90% yield; R_f = 0.75 (20:80 = EtOAc/n-Hexane); Yellow colored solid; mp: 95-98 ^oC; **FT-IR (neat)**: 3402, 2972, 2929, 2061, 1620, 1500, 1460, 1373, 1246, 1178, 1029, 808 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.37 (d, *J* = 8.3 Hz, 3H), 7.27-7.17 (m, 8H), 7.16-7.11 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 6.4 Hz, 1H), 6.40 (s, 1H), 6.16 (s, 1H), 5.65 (q, *J* = 7.1 Hz, 1H), 4.34 (d, *J* = 4.5 Hz, 1H), 3.86 (s, 3H), 1.81 (d, *J* = 7.1 Hz, 3H), 1.50 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 159.2, 141.7, 137.1, 130.5, 128.5, 128.5, 126.7, 126.0, 125.9, 120.8, 113.9, 110.3, 102.0, 55.3, 53.1, 18.2; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{31}H_{31}N_2O$: 447.2431; found: 447.2435.

Representative synthetic procedure for trifluoromehanesulfonylation of 4a:[15] To a stirred solution of **4a** (0.37 mmol, 106 mg) in dry CH_2Cl_2 (3 mL) at -40 ^oC, triethylamine (0.74 mmol, 0.1 mL) and tri-

fluoromehanesulfonicanhydride (0.56 mmol, 0.1 mL) was added. The reaction mixture was stirred for 12 h and then quenched with MeOH (1 mL). Solvents were evaporated under reduced pressure and, finally, purified by column chromatography over silica-gel to give the product **S4**.

1-Tosyl-1*H*-indol-6-yl trifluoromethanesulfonate (**S4**): 125 mg, 80% yield; R_f = 0.37 (20:80 = EtOAc/n-Hexane); Pink colored solid; mp: 67-68 ^oC; **FT-IR (neat)**: 3257, 2366, 2334, 1597, 1471, 1423, 1211, 1142, 934, 880, 674 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.97 (d, *J* = 1.3 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 3.6 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 146.7, 145.7, 134.6, 134.4, 130.4, 130.1, 128.4, 126.9, 122.5, 116.8, 108.7, 107.5, 21.6; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ, -72.64; **HR-MS (ESI, *m/z*)**: $[M+Na]^+$ calculated for $C_{16}H_{12}F_3NO_5$ Na S_2: 442.0001; found: 442.0007.

Representative synthetic procedure for the coupling with alkyne:[16] To an oven-dried round-bottomed flask, **S4** (0.2 mmol, 84 mg), phenylacetylene (0.24 mmol, 26 mg), $Pd(OAc)_2$ (5 mol %), PPh_3 (0.04 mmol, 11 mg), K_3PO_4 (0.22 mmol, 47 mg) and dry DMSO (1.6 mL) was added sequentially. The reaction mixture was allowed to run at 80 ^oC for 24 h and then the resulting mixture was allowed to cool down. The reaction mixture was extracted with diethyl ether (2 x 10 mL) and water (10 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Organic layer was removed under reduced pressure and, then, purified by column chromatography on silica-gel to yield the coupling product **7**.

6-(Phenylethynyl)-1-tosyl-1*H*-indole (**7**): 17 mg, 23% yield; R_f = 0.32 (10:90 = EtOAc/n-Hexane); Colorless thick liquid; **FT-IR (neat)**: 3063, 2918, 2360, 2342, 1732, 1598, 1427, 1374, 1173, 804 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 8.19 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.61-7.55 (m, 3H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.36 (ddd, *J* = 14.0, 5.6, 1.2 Hz, 4H), 7.23 (d, *J* = 9.5 Hz, 2H), 6.63 (d, *J* = 3.5 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 145.2, 135.2, 134.6, 131.6, 130.7, 130.0, 128.4, 128.3, 127.8, 127.5, 126.9, 126.84, 123.3, 121.3, 119.4, 116.8, 109.1, 90.0, 89.3, 21.6; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{23}H_{18}NO_2S$: 372.1053; found: 372.1073.

Representative synthetic procedure for arylation:[17] To an oven dried schlenk tube, **S4** (0.2 mmol, 84 mg, 1 equiv), phenyl boronic acid (0.24 mmol, 29 mg, 1.2 equiv), 5 mol % of tetrakistriphenylphosphenepalladium(0) (12 mg), $Ba(OH)_2.8H_2O$ (0.4 mmol, 126 mg, 2 equiv), 2 mL dimethoxyethane and 1.5 mL degassed water was added. The reaction was carried out at 80 ^oC for 18 h

and, then, cooled to room temperature. The reaction mixture was passed through a small pad of silica. The filtrate was purified by column chromatography on silica-gel to give the pure product **8**.

6-Phenyl-1-tosyl-1*H*-indole (**8**): 39 mg, 56% yield; R_f = 0.64 (10:90 = EtOAc/n-Hexane); Maroon colored solid; mp: 93-96 °C; **FT-IR (neat)**: 3141, 2984, 2854, 1597, 1470, 1421, 1371, 1275, 1173, 1127, 1092, 825, 674, 587 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 8.23 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.68-7.63 (m, 2H), 7.58 (dd, *J* = 7.7, 6.0 Hz, 2H), 7.51-7.43 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 3.5 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 145.0, 141.4, 138.2, 135.5, 135.4, 130.0, 129.9, 129.7, 128.9, 127.5, 127.3, 126.9, 126.8, 123.0, 121.6, 115.3, 112.1, 108.9, 21.6; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{21}H_{18}NO_2S$: 348.1053; found: 348.1053.

Representative synthetic procedure for esterification:[18] To a stirred solution of **4a** (0.2 mmol, 0.2 equiv) in dicholomethane (2 mL) at room temperature, triethylamine (0.3 mmol, 1.5 equiv), DMAP (0.02 mmol, 0.1 equiv) and trimethylacetylchloride (0.3 mmol, 1.5 equiv) was added. The reaction was stirred for 2 h and quenched with aq NH_4Cl. The crude reaction mixture was extracted with ethylacetate and purified by column chromatography over silica-gel to get the pure product **9**.

1-Tosyl-1*H*-indol-6-yl pivalate (**9**): 52 mg, 70% yield; R_f = 0.64 (30:70 = EtOAc/n-Hexane); white colored solid; mp: 80-84 °C; **FT-IR (neat)**: 976, 2923, 1748, 1476, 1373, 1271, 1173, 1112, 1000, 936, 813 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.83-7.74 (m, 3H), 7.54 (d, *J* = 3.7 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.96 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.64 (d, *J* = 3.7 Hz, 1H), 2.36 (s, 3H), 1.43 (s, 9H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 177.2, 148.6, 145.1, 135.1, 135.0, 130.0, 128.3, 126.8, 121.6, 117.7, 109.1, 107.3, 39.2, 27.2 (3C), 21.6; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{20}H_{22}NO_4S$: 372.1264; found: 372.1275.

Representative synthetic procedure for oxidative dearomatization:[19,20] Sodium cyanoborohydride (0.64 mmol, 40 mg) was added to a stirred solution of **5c** (0.2 mmol, 50 mg) in glacial acetic acid (1.5 mL) in an ice bath and stirred for 2 h at room temperature. Upon completion of the reaction (monitored by TLC analysis), the reaction vessel was cooled in ice bath and basified with the aqueous sodiumbicarbonate solution. After that, the reaction mixture was extracted with diehtylether. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography on silaca-gel to gave the product **11**.

To a stirred solution of **11** (0.2 mmol, 1 equiv) in AcCN:MeOH (9:1, 2 mL) at 0 °C, diacetoxyiodobenzene (0.22 mmol, 1.1 equiv) was added and stirred for 10 min. After completion of the starting material (based on TLC analysis), solvents were removed under reduced pressure. The crude

residue was purified by column chromatography on silica gel to gave the pure compound **10b**. Similarly, compound **10a** was prepared.

1-Benzyl-3a-methoxy-1,2,3,3a-tetrahydro-6*H*-indol-6-one (**10a**): 31 mg, 60% yield; R_f = 0.32 (60:40 = EtOAc/n-Hexane); Brown coloured semi solid; **FT-IR (neat)**: 2929, 2364, 2340, 1640, 1559, 1295, 1247, 1083, 1050, 828 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.38-7.26 (m, 3H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.42-6.24 (m, 2H), 5.39 (s, 1H), 4.46 (d, *J* = 15.5 Hz, 1H), 4.34 (d, *J* = 15.5 Hz, 1H), 3.87 (td, *J* = 9.6, 5.2 Hz, 1H), 3.30 (dd, *J* = 9.8, 8.2 Hz, 1H), 3.09 (s, 3H), 2.23 (dd, *J* = 12.6, 5.1 Hz, 1H), 2.05-1.99 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 185.4, 164.2, 135.5, 134.4, 134.2, 129.0, 128.0, 127.3, 93.8, 78.7, 51.5, 51.1, 49.9, 35.4; **DEPT-135 ^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 134.4, 134.2, 129.0, 128.0, 127.3, 93.8, 51.5, 51.1, 49.9, 35.4; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{16}H_{18}NO_2$: 256.1332; found: 256.1338.

3a-Methoxy-1-((S)-1-phenylethyl)-1,2,3,3a-tetrahydro-6*H*-indol-6-one (**10b**): (**dr 1.8:1**) 16 mg, 30% yield; R_f = 0.18 (30:70 = EtOAc/n-Hexane); Dark green colored semi solid; **FT-IR (neat)**: 2922, 2847, 2360, 2334, 1643, 1358, 1248, 1261, 1207, 1157, 1083, 831 cm^{-1}; **Major Diastereomer**: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.36-7.30 (m, 2H), 7.30-7.25 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.31 (d, *J* = 2.5 Hz, 2H), 5.42 (s, 1H), 4.98-4.86 (m, 1H), 3.75 (td, *J* = 9.6, 5.0 Hz, 1H), 3.19-3.13 (m, 1H), 3.11 (s, 3H), 2.19 (ddd, *J* = 17.7, 9.5, 4.9 Hz, 1H), 1.92-1.82 (m, 1H), 1.61 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 185.4, 175.1, 163.86, 140.5, 139.1, 134.4, 134.3, 134.2, 134.1, 128.9, 128.8, 128.0, 127.8, 126.7, 126.3, 94.0, 78.8, 53.2, 51.1, 46.4, 34.9, 20.7, 17.5; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{17}H_{20}NO_2$: 270.1489; found: 270.1502.

Minor Diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.37-7.30 (m, 2H), 7.30-7.26 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.31 (d, *J* = 2.5 Hz, 2H), 5.35 (s, 1H), 4.81 (q, *J* = 7.0 Hz, 1H), 3.63 (td, *J* = 9.7, 5.1 Hz, 1H), 3.45 (dd, *J* = 9.9, 8.2 Hz, 1H), 3.01 (s, 3H), 2.19 (ddd, *J* = 17.7, 9.5, 4.9 Hz, 1H), 1.98 (ddd, *J* = 12.6, 11.4, 7.1 Hz, 1H), 1.58 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 185.4, 175.1, 163.9, 140.5, 139.1, 134.4, 134.3, 134.2, 134.1, 128.9, 128.8, 128.0, 127.8, 126.7, 126.3, 94.4, 78.7, 53.5, 51.0, 47.1, 34.9, 20.7, 17.3.

2-Methyl-1-((R)-1-phenylethyl)indolin-6-ol (**11**) (**dr 3:1**): 40 mg, 80% yield; R_f = 0.4 (20:80 = EtOAc/n-Hexane); Maroon coloured liquid; **FT-IR (neat)**: 2975, 2933, 2852, 2360, 2347, 1616, 1473, 1263, 1193, 1042, 750 cm^{-1}; **Major Diastereomer**: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.45 (d, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 12.8, 5.0 Hz, 2H), 7.24 (dd, *J* = 8.2, 5.3 Hz, 1H), 6.81 (dd, *J* = 7.6, 4.0 Hz, 1H), 6.02 (d, *J* = 5.9 Hz, 1H), 5.55 (s, 1H), 4.52 (dd, *J* = 13.7, 6.9 Hz, 1H), 3.93-3.68 (m, 1H), 3.09 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.70 – 2.39 (m, 1H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.34 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR (101**

MHz, $CDCl_3$): δ, 155.1, 128.5, 128.3, 127.0, 126.9, 126.8, 124.3, 58.9, 36.6, 20.9, 16.5, 14.0; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{17}H_{20}NO$: 254.1539; found: 254.1551.

Minor Diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.39 (d, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 12.8, 5.0 Hz, 2H), 7.28-7.22 (m, 1H), 6.81 (dd, *J* = 7.6, 4.0 Hz, 1H), 6.02 (d, *J* = 5.9 Hz, 1H), 5.55 (s, 1H), 4.68 (dd, *J* = 14.1, 7.0 Hz, 1H), 4.12-3.95 (m, 1H), 3.09 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.63-2.43 (m, 1H), 1.62 (d, *J* = 7.1 Hz, 3H), 1.34 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 184.6, 155.1, 128.5, 128.3, 127.0, 126.9, 126.8, 124.3, 62.0, 37.0, 20.9, 16.5, 14.1.

Representative synthetic procedure for methylation: Sodium hydride (0.24 mmol, 10 mg) was added to compound **4a** placed in an oven-dried round-bottomed flask under N_2 in dry THF (2 mL) at 0 ^oC. The reaction was stirred for 10 min at the same temperature. To this, iodomethane (0.24 mmol, 15 µL) was added and stirred for overnight at room temperature. After completion of the starting material (based on TLC analysis), the reaction was quenched with aq NH_4Cl and extracted with ethylacetate (10 mL x 2). Further, combined organic layers was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. Finally, the residue was purified by column chromatography on silica gel to give compound **12**.

6-Methoxy-1-tosyl-1*H*-indole (**12**): 58 mg, 96% yield; R_f = 0.32 (30:70 = EtOAc/n-Hexane); White colored solid; mp: 65-67 ^oC; **FT-IR (neat)**: 2918, 2362, 1998, 1620, 1576, 1484, 1362, 1280, 1172, 875, 803 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.73 (d, *J* = 8.1 Hz, 2H), 7.52 (s, 1H), 7.43 (d, *J* = 3.5 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.24-7.17 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.56 (d, *J* = 3.5 Hz, 1H), 3.86 (s, 3H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 157.9, 144.9, 135.9, 135.3, 129.9, 126.8, 125.1, 124.5, 121.8, 112.5, 109.0, 97.9, 55.8, 21.6; **HR-MS (ESI, *m/z*)**: $[M+Na]^+$ calculated for $C_{16}H_{15}NO_3NaS$: 324.0665; found: 324.0676.

Representative synthetic procedure for TBDMS protection: To a stirred solution of **3u** (307 mg, 1.32 mmol) in dry dichloromethane under N_2 atmosphere, imidazole (99 mg, 1.45 mmol) and TBDMSCl (219 mg, 1.45 mmol) was added. The reaction was stirred for 3 h at room temperature. After completion of starting material (based on TLC analysis), the reaction was quenched with water and extracted with dichloromethane (10 mL x 2). Combined organic layers dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by column chromatography on silica-gel to give product **S5**.

Ethyl 2-(6-((tert-butyldimethylsilyl)oxy)-2-methyl-1*H*-indol-1-yl)acetate (**13**): 340 mg, 77% yield; R_f = 0.7 (20:80 = EtOAc/n-Hexane); Light yellow colored liquid; **FT-IR (neat)**: 2957, 2859, 1748, 1621, 1521, 1486, 1472, 1398, 1261, 1197, 906, 894 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.36 (d, *J* =

8.3 Hz, 1H), 6.68 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 6.27-6.20 (m, 1H), 4.72 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.03 (s, 9H), 0.22 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 168.8, 151.1, 138.0, 135.5, 122.9, 120.1, 113.9, 100.6, 99.8, 61.6, 44.9, 25.8, 25.7, 18.3, 14.2, 12.5, -4.4; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{19}H_{30}NO_3Si$: 348.1989; found: 348.1999.

Representative synthetic procedure for reduction of ester: To a stirred solution of **S5** (300 mg, 0.9 mmol) in dry diethyl ether (4 mL) at 0 °C, $LiAlH_4$ (72 mg, 1.89 mmol) was added in portion wise. The reaction mixture was stirred for 30 min at the same temperature. After complete comsumption of starting material (on the basis of TLC analysis), reaction was quenched by a few drops of aq $NaHCO_3$ until a clear solution was obtained. The clear solution was decanned and dried over anhydrous Na_2SO_4. Combined organic layers were evaporated under reduced pressure to gave pure product **S6** without further purification.

2-(6-((tert-Butyldimethylsilyl)oxy)-2-methyl-1*H*-indol-1-yl)ethan-1-ol (**14**): 270 mg, 88% yield; R_f = 0.32 (20:80 = EtOAc/n-Hexane); Colourless liquid; **FT-IR (neat)**: 3394, 2950, 2930, 2859, 2358, 1615, 1506, 1485, 1253, 1201, 1076, 977, 839 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 7.34 (d, *J* = 8.4 Hz, 1H), 6.77 (s, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.18 (s, 1H), 4.17 (t, *J* = 5.5 Hz, 2H), 3.91 (t, *J* = 5.4 Hz, 2H), 2.43 (s, 3H), 1.03 (s, 9H), 0.23 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ, 150.8, 137.6, 136.0, 122.9, 119.9, 113.8, 100.2, 100.0, 61.7, 45.4, 25.8, 18.3, 12.9, -4.4; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_{17}H_{28}NO_2Si$: 306.1884; found: 306.1895.

Representative synthetic procedure for cascade fluorination and cyclization:[21] To a substrate **S6** (34 mg, 0.10 mmol), selectfluor (71 mg, 0.2 mmol), $NaHCO_3$ (8.4 mg, 0.1 mmol) in a 10 mL Schlenk tube at 0 °C, MeCN (1.0 mL) was added and the reaction mixture was stirred at 0 ºC under N_2 for 30 min. On completion of the starting material (monitored by TLC), the reaction was quenched with Et_3N (0.2 mL). The crude product was purified by column chromatography on silica-gel to give the pure product **13**.

6-((*tert*-Butyldimethylsilyl)oxy)-9,9-difluoro-9a-methyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (**15**): 32 mg, 94% yield; R_f = 0.4 (10:90 = EtOAc/n-Hexane); colourless liquid; **FT-IR (neat)**: 2958, 2930, 2858, 2363, 1734, 1615, 1494, 1471, 1261, 1101, 1065, 983, 784 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)**: δ, 7.33 (d, *J* = 8.2 Hz, 1H), 6.52 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.33 (d, *J* = 1.5 Hz, 1H), 4.04 (td, *J* = 7.4, 2.1 Hz, 1H), 3.71 (ddd, *J* = 9.9, 8.0, 6.2 Hz, 1H), 3.58 (ddt, *J* = 10.5, 6.1, 2.1 Hz, 1H), 3.51 (ddd, *J* = 11.8, 10.0, 6.9 Hz, 1H), 1.58 (d, *J* = 1.0 Hz, 3H), 1.01 (s, 9H), 0.24 (d, *J* = 1.5 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ, 160.5, 125.2, 114.9, 105.4, 65.9, 50.7, 29.7, 25.6, 18.6, 18.5, 18.2, -4.4; **^{19}F NMR (471 MHz, $CDCl_3$)**: δ, -95.6, -96.1, -105.4, -105.9; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for

$C_{17}H_{26}NO_2SiF_2$: 342.1695; found: 342.1665.

Representative synthetic procedure for detosylation:[22] To a compound **12** (0.2 mmol, 60 mg) in methanol (2 ml), Mg granules (50 mesh, 3.6 mmol, 86 mg) was added and then mixture was sonicated for 1.5 h at room temperature. Reaction mixture was diluted with dichloromethane, washed with 1N HCl followed by aqueous $NaHCO_3$ and dried over Na_2SO_4**.** Reamaining residue was purified by coloumn chromatography over silica gel to get compound **14**.

6-Methoxy-1*H*-indole (16): 28 mg, 96% yield; R_f = 0.33 (20:80 = EtOAc/n-Hexane); White coloured semi solid; **FT-IR (neat)**: 3396, 2918, 2850, 1633, 1296, 1250, 1161, 1027, 943, 811, 714 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ, 8.01 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.08 (s, 1H), 6.87 (s, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.47 (s, 1H), 3.84 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ, 156.5, 136.5, 123.0, 122.2, 121.3, 109.9, 102.5, 94.5, 55.7; **HR-MS (ESI, *m/z*)**: $[M+H]^+$ calculated for $C_9H_{10}NO$: 148.0757; found: 48.0783.

ASSOCIATED CONTENT

Supporting Information

The copies of ^{1}H and ^{13}C NMR spectra for all products. The Supporting Information is available free of charge on the ACS Publications website.

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