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An Efficient Approach to Functionalized Indoles from λ3-Iodanes via Acyloxylation and Acyl Transfer

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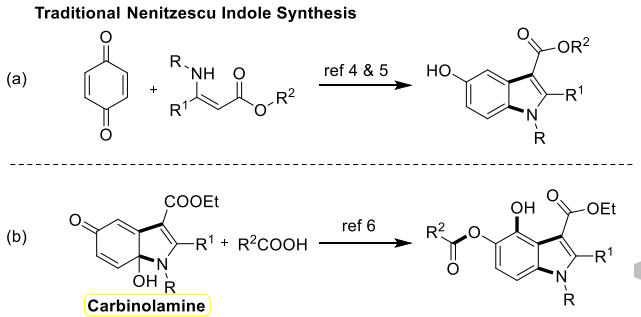
Abstract. Versatile role of λ3-iodanes has been identified between the reaction of hydroquinone and β-enaminones for the synthesis of 5-acyloxy-4-hydroxy indoles. The reaction is proposed to proceed through an intermolecular C-C bond formation, intramolecular cyclization, acyloxylation and 1,4-acyl migration. The important features of this work include various acyloxylation from λ3-iodanes and broad functional group tolerance to deliver 34 examples in moderate to good yields.

Keywords: Hydroxy indoles; λ3-iodane; Nenitzescu; acyloxylation; 1,4-acyl migration

Introduction

Indoles are the most abundant class of heterocycles found in natural products and pharmaceuticals.[1] In particular, 5-hydroxy indoles and its methoxy derivatives are known to exhibit excellent biological acitivties.[2,3] For examples, serotonin is an important neurotransmitter in the central nervous system,[3a] roxindole used in the treatment of schizophrenia,[3b] and arbidol is used as an antiviral drug.[3c] In 1929, Costin Nenitzescu discovered a reaction between *p*-benzoquinone and β-enaminoesters to synthesize 5-hydroxy indoles and named it as Nenitzescu indole synthesis (Scheme 1a).[4]

Since its discovery, several researchers have made significant efforts to develop new reaction conditions for the Nenitzescu synthesis.[5] In this context, Kuckländer et al reported the reaction of *p*-benzoquinone with β-enaminoesters using glacial acetic to produce 5-acetoxy-4-hydroxy-indole albeit in low yield.[6a] Subsequent studies revealed that the carbinolamine formed in the Nenitzescu indole synthesis was the key starting material to afford 5-acetoxy-4-hydroxy-indoles with the external organic acids (Scheme 1b).[6] However, the poor substrate scope of acids and preparation of carbinolamine as a starting material has limited the scope of this methodology. Therefore, the development of new synthetic transformations that allow known structures to be made more efficiently using reagents that have ready accessibility, high reactivity, impressive functional group tolerance, reduced toxicity and environmentally benign nature is a significant area of research.[7]

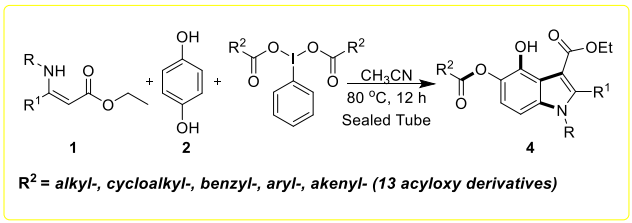


Scheme 1. Previous work on the hydroxy indole synthesis

Polyvalent iodine chemistry have become a versatile and highly valuable tool in the organic synthesis for the construction of a plethora of bioactive natural products and heterocycles.[8] For instances, (diacetoxyiodo)benzene (PIDA) or (bis(trifluoroacetoxy)iodo)benzene (PIFA) have become important reagent for the construction of N-N,

N-S, N-C and C-C bond formations under metal-free conditions[9,10] On the other hand, several useful methodologies have been reported for the acetoxylation of Csp^2-H/Csp^3-H bonds under transition-metals and metal-free reaction conditions using iodobenzene diacetate,[11,12] and other acetoxylation agents[11g,13] However, to date there is no report using λ^3-iodanes to achieve heterocyclic ring formation, aromatic Csp^2-H bond acyloxylation and acyl migration in a cascade manner.

Herein, we report the synthesis of 5-acyloxy-4-hydroxy-indoles in a one-pot fashion from hydroquinone and β-enaminones (Scheme 2) through a hypervalent iodine mediated C-C bond formation, intramolecular cyclization, acyloxylation and aromative 1,4-acyl migration.



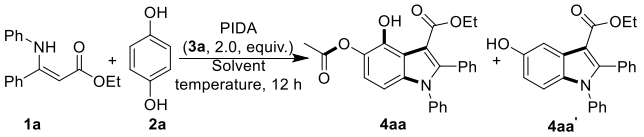
Scheme 2. This work on acyloxy-hydroxy indole synthesis

Results and Discussion

The initial studies of this methodology was began using ethyl-3-phenyl-3-(phenylamino) acrylate **1a**, hydroquinone **2a** and iodobenzene diacetate (PIDA) **3a** in 1,4 dioxane at room temperature under air for 12 h (Table 1). Interestingly, the 5-acetoxy-4-hydroxy indole compound **4aa** was obtained in 25% yield (Table 1, entry 1). Changing the solvent from 1,4-dioxane to other solvents like trifluorotoluene, THF, CH_3CN, 1,2-DCE, DCM, DMF, DMSO, CH_3NO_2 and MeOH (Table 1, entries 2-10) disclosed CH_3CN as the choice of solvent by affording compound **4aa** in 42% yield along with traces of hydroxy indole **4aa'** (Table 1, entry 3). Increasing the temperature to 80 °C slightly improved the yield of **4aa** and 10% of **4aa'** (Table 1, entry 11). The structure of compound **4aa** and **4aa'** was confirmed by X-ray analysis.[14]

No substantial improvement in the yield under oxygen and nitrogen atmosphere as compared to open air (Table 1, entries 12-13). Surprisingly, compound **4aa** was produced in 88% yield when the reaction was performed in a sealed tube with traces of **4aa'** (Table 1, entry 14). The probable reason for the yield improvement can be attributed to the pressure developed inside the sealed tube. Either decreasing or increasing the reaction temperature led to a lower reaction yield (Table 1, entries 15-16). Replacing, PIDA with electron donating and electron-withdrawing λ^3-iodanes did not improve the yield of **4aa** (Table 1, entries 17-18). Thus of the conditions screened, Table 1, entry 14 is chosen as the optimized conditions for further studies.

Table 1. Optimization Studies[a)]



entry	solvents	temperature °C	yield[b)]	
			4aa	**4aa'**
1	1,4-dioxane	rt	25	-
2	Trifluorotoluene	rt	37	-
3	THF	rt	32	-
4	CH_3CN	rt	42	traces
5	1,2-DCE	rt	36	-
6	DCM	rt	38	-
7	DMF	rt	-	-
8	DMSO	rt	-	-
9	Nitromethane	rt	24	-
10	MeOH	rt	24	-
11	CH_3CN	80	50	10
12[c)]	CH_3CN	80	52	12
13[d)]	CH_3CN	80	51	9
14[e)]	**CH_3CN**	**80**	**88**	**traces**
15[e)]	CH_3CN	60	80	traces
16[e)]	CH_3CN	100	75	traces
17[e,f)]	CH_3CN	80	84	traces
18[e,g)]	CH_3CN	80	82	traces

[a)] All reactions were carried out using **1a** (0.25mmol), **2a** (0.5 mmol) and **3a** (0.5 mmol) in solvent (0.15 M) for 12 h under air at indicated temperature unless otherwise noted. [b)] Isolated yield. [c)] Reaction was performed under O_2 atmosphere. [d)] Reaction was performed under N_2 atmosphere. [e)] Reaction was performed in a sealed tube. [f)] 1-(diacetoxyiodo)-4-methylbenzene was used instead of PIDA. [g)] 4-(diacetoxyiodo)benzonitrile was used instead of PIDA. Traces refers to less than 5% of **4aa'**

The scope and limitations of this work were tested by performing the acyloxylation and 1,4-acyl migration under the optimized conditions with 15 different λ^3-iodane derivatives (Table 2). A series of λ^3-iodanes functionalities on R^2 group like ethyl- (**3b**) tert-butyl- (**3c**), cyclohexyl- (**3d**), and methylcyclohexyl- (**3e**) were reacted with ethyl-3-phenyl-3-(phenylamino) acrylate **1a** and hydroquinone **2a**. The desired products **4ab-ae** were obtained smoothly in 65-79% yields. The structure of compound **4ab** was confirmed unambiguously with the help of single crystal X-ray analysis (Fig.1).[14] Then, the feasibility of the reaction was examined with phenyl (**3f**), 3-MeO-C_6H_4- (**3g**), 4-MeO-C_6H_4- (**3h**) and 4-NO_2-C_6H_4- (**3i**). The reaction worked in all the cases irrespective or electronic and steric factors to afford the required products **4af-ai** in 60-71% yields. Of note, the reaction worked well with benzyl (**3j**), but-1-enyl- (**3k**) cinnamyl- (**3l**) and FMOC-NH-CH_2- (**3m**) to produce the desired product **4aj-am** in 40-81% yields. However, the reaction did not create

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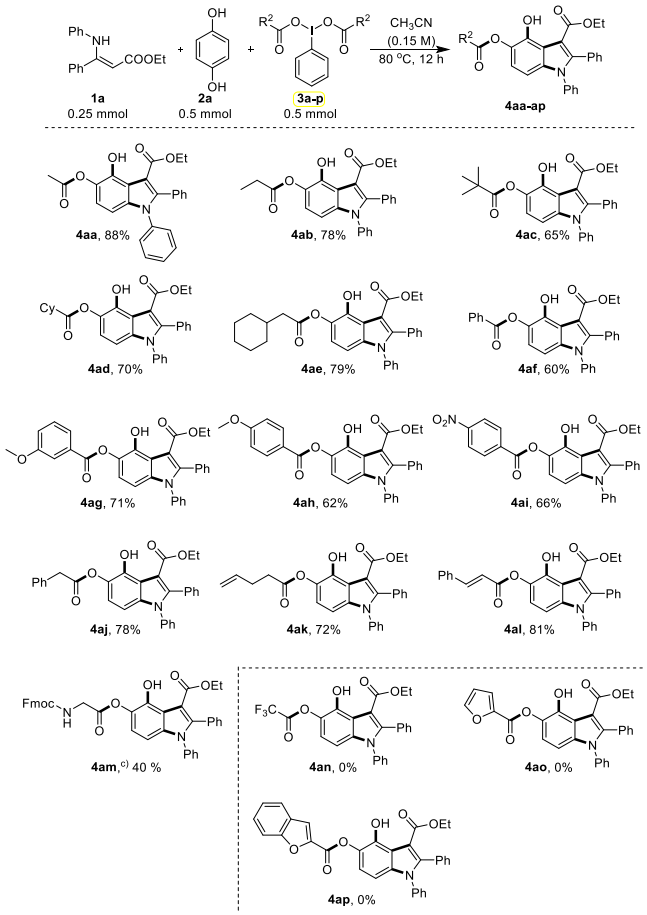
the acyloxylation products **4an**-**4ao** with trifluoro- (**3n**), 2-furanyl- (**3o**) and 2-benzofuranyl- (**3p**).

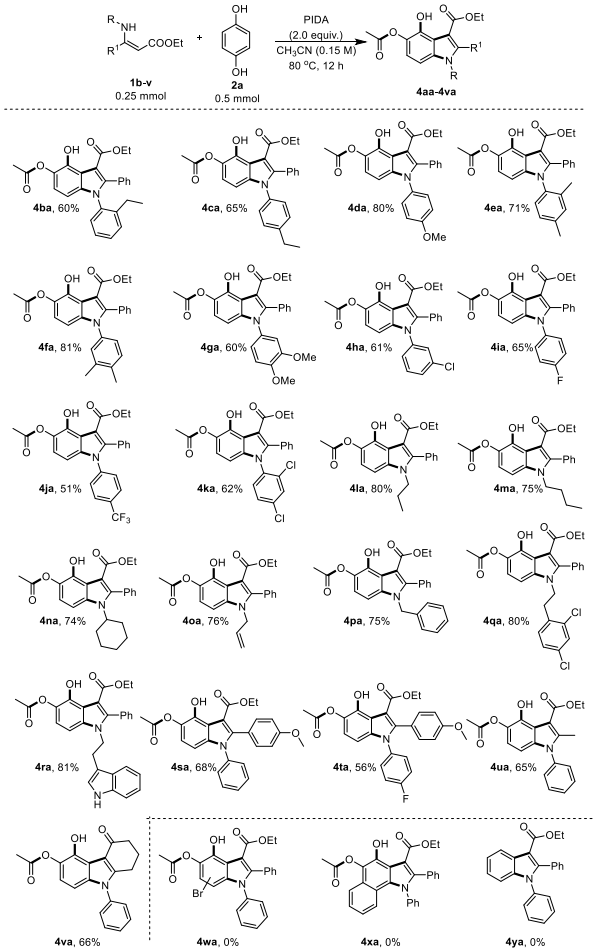
Table 2. Scope and limitations of λ^3-Iodanes for acyloxylation and 1,4-acyl migration[a,b]



[a] Reactions was performed in sealed tube. [b] Isolated yields. [c] Fluorenylmethyloxycarbonyl (Fmoc)

To illustrate the generality of this methodology, a series of N-substituted β-enaminones **1b-v** were reacted with hydroquinones **2a-d** and PIDA **3a** under the standard reaction conditions (Table 3). An array of ethyl 5-acetoxy-4-hydroxy-1*H*-indole-3-carboxylate derivatives **4ba-ya** was obtained in 51-81% yields. The reaction proceeded smoothly with R-functionalities like 2-Et-Ph- (**1b**), 4-Et-Ph- (**1c**), 4-MeO-Ph- (**1d**), 2,4-di-Me-Ph- (**1e**), 3,4-di-Me-Ph- (**1f**), 3,4-di-MeO-Ph- (**1g**) to afford product **4ba-ga** in 60%-81% yields. When the phenyl group on R-functionality was attached with halogens like 3-Cl- (**1h**), 4-F- (**1i**), 4-CF_3- (**1j**), and 2,4-di-Cl- (**1k**) the yields were slightly suppressed. The reaction underwent smooth conversion with the R- groups bearing aliphatic substrates such as *n*-propyl- (**1l**), *n*-butyl- (**1m**) and cyclohexyl- (**1n**) to afford the desired compounds **4la-na** in 74-80% yields. Further scrutinization of R- groups bearing allyl- (**1o**), benzyl- (**1p**), aryl ethyl- (**1q**) and 2-(1*H*-Indol-1-yl) ethyl- (**1r**) groups also delivered the expected products in 75-81% yields. Next, the scope of R^1- was investigated by replacing the phenyl group with 4-methoxy phenyl- (**1t**) and methyl- (**1u**). The reaction proceeded finely to afford the corresponding compounds **4ta** and **4ua** in 56-68% yields. By utilizing this strategy, the synthesis of tetrahydrocarbazole framework **4va** was successfully accomplished with 66% yield using cyclic β-enaminones **1v**. However, the reaction failed to form the products **4wa-ya** using 2-bromobenzene-1,4-diol (**2b**), 1,4-dihydroxynaphthalene (**2c**) and phenol (**2d**). The probable reason could be the rapid decomposition of the substrates under the standard conditions. In general, N-alkyl enaminoesters gave better reaction yields than N-aryl enaminoesters.

Table 3. Scope and limitations of β-enaminones[a,b]



[a] Reaction Conditions: Reactions was performed in sealed tube. [b] Isolated yields.

To gain insights into the reaction mechanisms, few control studies were performed as presented in Scheme 3. Radical inhibition studies using TEMPO (2.0 equiv.) and 1, 4-cyclohexadiene (CHD) (2.0 equiv.) under standard conditions gave the desired compound **4aa** in 71% and 67% yields suggesting that the reaction proceeds via a non-radical pathway (Scheme 3a). Next, reaction was performed with benzoquinone **2a'** under the standard reaction

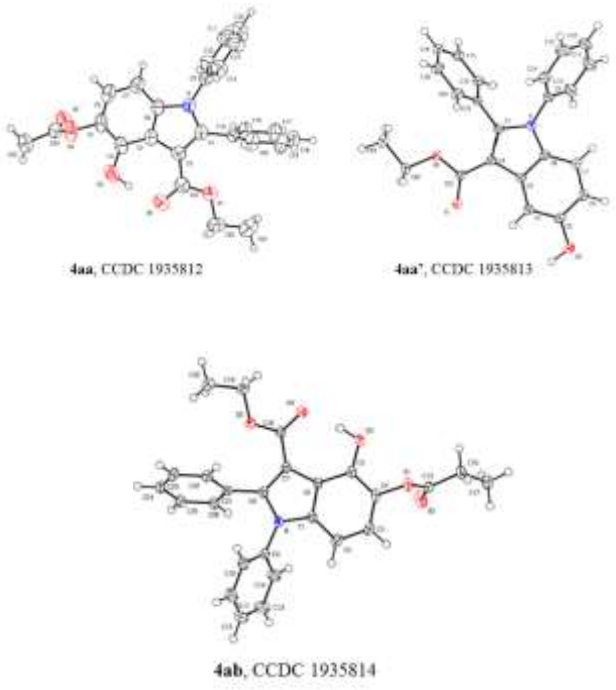
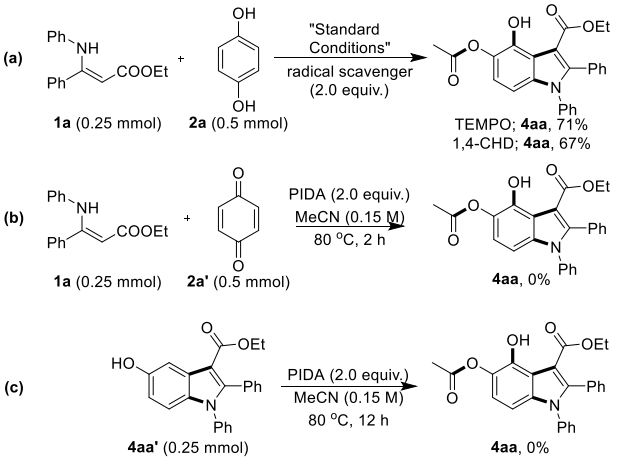


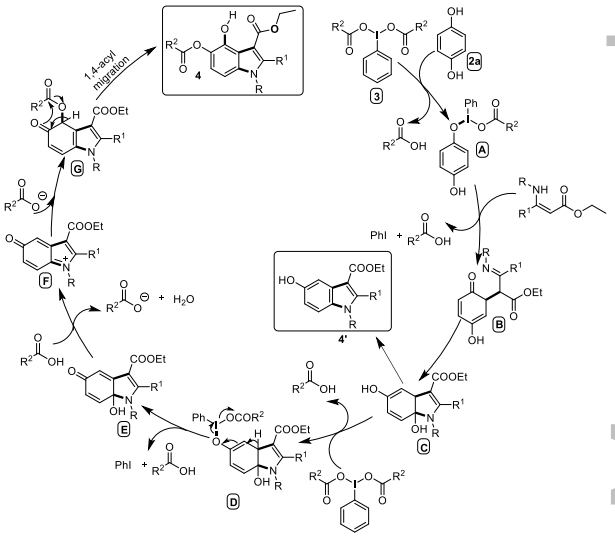
Figure 1. X-ray data for compounds **4aa, 4aa'** and **4ab**

conditions, considering that hydroquinone can undergo oxidation to benzoquinone using PIDA.[15] (Scheme 2b). But the desired product **4aa** was not formed, instead an intramolecular cyclization reaction of β-enaminoester resulted in the formation of indole.[9f,16] When the reaction was carried out with hydroxy indole **4aa'** under the standard conditions, the expected acyloxy-hydroxy-indole **4aa** was not formed (Scheme 2c). This results suggest that the Nenitzescu product **4aa'** was not the desired intermediate.



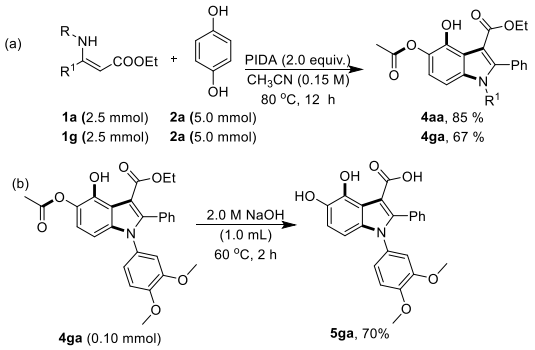
Scheme 3. Control Experiments

A plausible mechanism was proposed in Scheme 4 based on the control experiments. The initial electrophilic substitution of hydroquinone to λ^3-iodane gave the intermediate **A**.[17] Subsequent reaction of intermediate **A** with β-enaminones **1** resulted in the C-C bond intermediate **B**.[17] Intramolecular cyclization of **B** followed by electrophilic substitution of hydroxy intermediate **C** to λ^3-iodane produced the intermediate **D**. Elimination of iodobenzene and acid from **D** afforded the carbinolamine intermediate 7a-hydroxy-dihyroindole compound **E**. Acid mediated elimination of water followed by an in situ aza Michael attack of carboxylate ion produced the 4-acyloxy product **G**[6] through intermediate **F**. Aromative 1,4-acyl migration of intermediate **G** afforded the 5-acyloxy-4-hydroxy indole derivatives **4**. The probable reason for these migration may be attributed to the formation of stable hydrogen bonding with the ester group.[6]



Scheme 4. Plausible Mechanistic Rationale

The synthetic feasibility of the reaction has been demonstrated on a 2.5 mmol scale for the synthesis of compound **4aa** and **4ga** under the standard conditions as shown in Scheme 5a. The reaction proceeded smoothly in both the cases with no loss in the product yields. The synthetic application has been extended to synthesize bioactive dihydroxy indoles.[18] As a proof of concept, compound **5ga** was prepared under basic hydrolysis of **4ga** (Scheme 5b).



Scheme 5. Scaleup Feasibility and Hydrolysis Reactions

Conclusion

We have developed an efficient method for the synthesis of 5-acyloxy-4-hydroxy indoles from hydroquinone and β-enaminones with λ^3-iodanes. Control experiment studies were useful in proposing a new reaction pathway for the first time using λ^3-iodanes. Thirteen acyloxy functional group transfer followed by acyl migration with different electronic and steric properties has been accomplished. The synthetic utility of the product was extended by preparing 4,5-dihydroxy indole through ester hydrolysis.

Experimental Section

To the stirred solution of **1a-v** (0.25 mmol, 1.0 equiv.) and **2a-d** (0.5 mmol, 2.0 equiv.) in 0.15 M of acetonitrile was added **3a-p** (0.5 mmol, 2.0 equiv.) at room temperature and the mixture was heated at 80 °C in a sealed tube. After completion by TLC, the reaction mixture was diluted with water and extracted with ethylacetate. Combined organic layer was washed with water, brine, dried over sodium sulfate and evaporated under reduced pressure. The obtained crude products were purified by column chromatography using ethyl acetate and hexane as the eluent to afford the pure compounds **4aa**-**4ya**.

Ethyl 5-acetoxy-4-hydroxy-1,2-diphenyl-1*H*-indole-3-carboxylate (4aa). Following the general procedure, the title compound was obtain as a white solid. (84 mg, yield = 88 %); Mp. 168-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.38 – 7.29 (m, 3H), 7.30 – 7.17 (m, 6H), 7.17 – 7.10 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.98, 168.37, 146.59, 142.59, 137.28, 136.39, 132.53, 131.44, 130.65, 129.18, 128.42, 128.37, 128.35, 127.34, 119.61, 116.27, 106.26, 101.63, 61.07, 20.79, 13.37; HRMS (EI) $[M]^+$ calcd. for $C_{25}H_{21}NO_5$: 415.1420, found 415.1425.

Ethyl 4-hydroxy-1,2-diphenyl-5-(propionyloxy)-1*H*-indole-3-carboxylate (4ab). Following the general procedure, the title compound was obtain as a brown solid. (83 mg, yield = 78 %); Mp. 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 7.36 – 7.28 (m, 3H), 7.28 – 7.16 (m, 5H), 7.15 – 7.11 (m, 2H), 6.93 (dd, *J* = 8.7, 0.5 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.76 – 2.62 (m, 2H), 1.32 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.40, 168.36, 146.52, 142.60, 137.23, 136.42, 132.60, 131.47, 130.67, 129.16, 128.40, 128.36, 127.33, 119.66, 116.28, 106.24, 101.57, 61.04, 27.45, 13.37, 9.29; HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{24}NO_5$: 430.1649, found 430.1651.

Ethyl 4-hydroxy-1,2-diphenyl-5-(pivaloyloxy)-1*H*-indole-3-carboxylate (4ac). Following the general procedure, the title compound was obtain as an off white solid. (74 mg, yield = 65 %); Mp. 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.19 (m, 5H), 7.17 – 7.12 (m, 2H), 6.90 (d, *J* = 8.7, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.45 (s, 9H), 0.89 (t, *J* = 7.6, 3H); ^{13}C NMR (100 MHz, cdcl$_3$) δ 177.42, 168.34, 146.41, 142.66, 137.19, 136.49, 132.90, 131.53, 130.71, 129.15, 128.39, 128.37, 128.30, 127.31, 119.64, 116.31, 106.20, 101.43, 60.99, 39.09, 27.36, 13.39; HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{28}NO_5$: 458.1962, found 458.1961.

Ethyl 5-((cyclohexanecarbonyl)oxy)-4-hydroxy-1,2-diphenyl-1*H*-indole-3-carboxylate (4ad). Following the general procedure, the title compound was obtain as a brown solid. (84 mg, yield = 70 %); Mp. 145-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 7.38 – 7.30 (m, 3H), 7.31 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 7.15 (ddd, *J* = 6.5, 4.6, 2.9 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.71 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.24 – 2.12 (m, 2H), 1.93 – 1.82 (m, 2H), 1.73 (dd, *J* = 19.3, 7.6 Hz, 3H), 1.49 – 1.23 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.95, 168.35, 146.45, 142.62, 137.19, 136.46, 132.66, 131.51, 130.69, 129.15, 128.37, 128.32, 127.32, 119.72, 116.28, 106.21, 101.49, 61.01, 43.12, 29.14, 28.80, 25.83, 25.66, 25.45, 25.31, 13.38; HRMS (ESI): $[M+H]^+$ calcd. for $C_{30}H_{30}NO_5$: 484.2118, found 484.2116.

Ethyl 5-(2-cyclohexylacetoxy)-4-hydroxy-1,2-diphenyl-1*H*-indole-3-carboxylate (4ae). Following the general procedure, the title compound was obtain as a brown solid. (98 mg, yield = 79 %); Mp. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 – 11.22 (s, 1H), 7.43 – 7.10 (m, 10H), 6.96 – 6.89 (m, 1H), 6.58 (d, J = 8.7 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.55 (d, J = 7.0 Hz, 2H), 2.14 – 1.88 (m, 3H), 1.86 – 1.64 (m, 4H), 1.46 – 1.03 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.95, 168.38, 146.51, 142.67, 137.23, 136.42, 132.56, 131.48, 130.68, 129.17, 128.40, 128.37, 128.35, 127.33, 119.75, 116.27, 106.23, 101.54, 61.04, 42.01, 35.12, 33.04, 26.23, 26.11, 13.38; HRMS (ESI): $[M+H]^+$ calcd. for $C_{31}H_{32}NO_5$: 498.2275, found 498.2274.

Ethyl 5-(benzoyloxy)-4-hydroxy-1,2-diphenyl-1*H*-indole-3-carboxylate (4af). Following the general procedure, the title compound was obtain as a brown solid. (71 mg, yield = 60 %); Mp. 213-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (d, *J* = 0.4 Hz, 1H), 8.37 – 8.25 (m, 2H), 7.66 – 7.59 (m, 1H), 7.56 – 7.48 (m, 2H), 7.38 – 7.29 (m, 3H), 7.29 – 7.18 (m, 6H), 7.18 – 7.13 (m, 2H), 7.05 (dd, *J* = 8.7, 0.4 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 0.88 (dd, *J* = 9.3, 5.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.33, 165.52, 146.53, 142.83, 137.35, 136.45, 133.20, 132.68, 131.49, 130.70, 130.36, 129.80, 129.19, 128.39, 127.34, 119.74, 116.37, 106.32, 101.67, 61.05, 13.38; HRMS (ESI): $[M+H]^+$ calcd. for $C_{30}H_{24}NO_5$: 478.1649, found 478.1646.

Ethyl 4-hydroxy-5-((3-methoxybenzoyl)oxy)-1,2-diphenyl-1*H*-indole-3-carboxylate (4ag). Following the general procedure, the title compound was obtain as a brown solid. (89 mg, yield = 71 %); Mp. 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (t, *J* = 1.9 Hz, 1H), 7.99 – 7.88 (m, 1H), 7.83 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H), 7.26 – 7.22 (m, 3H), 7.22 – 7.15 (m, 4H), 7.09 – 7.03 (m, 1H), 6.62 (t, *J* = 9.7 Hz, 1H), 4.10 (dt, *J* = 10.2, 5.6 Hz, 2H), 3.91 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.32, 165.36, 159.56, 146.54, 142.82, 137.36, 136.45, 132.69, 131.48, 131.07, 130.70, 129.41, 129.19, 128.39, 128.37, 127.34, 122.88, 120.12, 119.69, 116.37, 114.37, 106.32, 101.67, 61.05, 55.50, 13.38; HRMS (ESI): $[M+H]^+$ calcd. for $C_{31}H_{26}NO_6$: 508.1754, found 508.1755.

Ethyl 4-hydroxy-5-((4-methoxybenzoyl)oxy)-1,2-diphenyl-1*H*-indole-3-carboxylate (4ah). Following the general procedure, the title compound was obtain as a brown solid. (78 mg, yield = 62 %); Mp. 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.06 (m, 1H), 7.91 – 7.78 (m, 2H), 7.42 – 7.30 (m, 2H), 7.25 – 7.19 (m, 3H), 7.07 – 7.01 (m, 2H), 6.88 – 6.82 (m, 2H), 6.66 – 6.60 (m, 2H), 4.27 (m, 2H), 3.83 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.70, 166.19, 165.76, 163.46, 150.92, 140.05, 134.14, 132.32, 131.94, 131.74, 129.28, 129.17, 129.12, 128.77, 128.59, 128.19, 122.80, 121.87, 121.77, 115.42, 113.81, 113.49, 74.75, 62.43, 60.40, 55.38, 30.30, 14.30; HRMS (ESI): $[M+H]^+$ calcd. for $C_{31}H_{26}NO_6$: 508.1754, found 508.1754.

Ethyl 4-hydroxy-5-((4-nitrobenzoyl)oxy)-1,2-diphenyl-1*H*-indole-3-carboxylate (4ai). Following the general procedure, the title compound was obtain as a brown solid. (86 mg, yield = 66 %); Mp. 215-217 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ 12.06 – 11.61 (m, 1H), 8.56 – 8.45 (m, 2H), 8.43 – 8.34 (m, 2H), 7.43 – 7.32 (m, 3H), 7.33 – 7.15 (m, 8H), 7.11 – 7.04 (m, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.38, 163.64, 150.68, 146.77, 142.63, 137.51, 136.32, 135.31, 132.32, 131.46, 131.31, 130.66, 129.25, 128.51, 128.48, 128.35, 127.39, 123.56, 119.23, 116.39, 106.34, 101.83, 61.17, 13.37. HRMS (ESI): $[M+H]^+$ calcd. for $C_{30}H_{23}N_2O_7$: 523.1499, found 523.1500.

Ethyl 4-hydroxy-1,2-diphenyl-5-(2-phenylacetoxy)-1*H*-indole-3-carboxylate (4aj). Following the general procedure, the title compound was obtain as an off white solid. (95 mg, yield = 78 %); Mp. 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.53 – 7.42 (m, 2H), 7.41 – 7.32 (m, 2H), 7.34 – 7.14 (m, 9H), 7.16 – 7.07 (m, 2H), 6.91 – 6.85 (m, 1H), 6.53 (d, *J* = 8.7 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.36, 168.36, 146.55, 142.64, 137.27, 136.38, 133.97, 132.60, 131.43, 130.66, 129.45, 129.16, 128.52, 128.41, 128.34, 127.33, 127.00, 119.53, 116.26, 106.24, 101.52, 61.06, 41.01, 13.37. HRMS (ESI): $[M+H]^+$ calcd. for $C_{31}H_{26}NO_5$: 492.1805, found 492.1805.

Ethyl 4-hydroxy-5-(pent-4-enoyloxy)-1,2-diphenyl-1*H*-indole-3-carboxylate (4ak). Following the general procedure, the title compound was obtain as an off white solid. (82 mg, yield = 72 %); Mp. 192-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.36 – 7.28 (m, 3H), 7.28 – 7.16 (m, 5H), 7.15 – 7.10 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 5.97 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.16 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.06 (ddd, *J* = 10.2, 2.9, 1.3 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.76 (dd, *J* = 8.2, 6.7 Hz, 2H), 2.58 (dt, *J* = 8.2, 6.6 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.95, 168.35, 146.54, 142.58, 137.23, 136.72, 136.38, 132.50, 131.42, 130.65, 129.16, 128.40, 128.34, 127.32, 119.62, 116.25, 115.55, 101.57, 61.04, 33.39, 29.09, 13.36. HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{26}NO_5$: 456.1805, found 456.1804.

Ethyl 5-(cinnamoyloxy)-4-hydroxy-1,2-diphenyl-1*H*-indole-3-carboxylate (4al). Following the general procedure, the title compound was obtain as an off white solid. (102 mg, yield = 81 %); Mp. 191-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.81 (s, 1H), 7.98 (d, *J* = 16.0 Hz, 1H), 7.63 (dt, *J* = 5.5, 3.6 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.39 – 7.31 (m, 3H), 7.31 – 7.20 (m, 5H), 7.20 – 7.14 (m, 2H), 7.07 – 7.02 (m, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.35, 165.80, 146.54, 146.19, 142.72, 137.30, 136.42, 134.47, 132.48, 131.47, 130.68, 130.37, 129.19, 128.87, 128.41, 128.37, 128.27, 127.34, 119.73, 117.45, 116.32, 106.31, 101.68, 13.37; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{32}H_{25}NNaO_5$: 526.1624, found 526.1625.

Ethyl 5-(((((9H-fluoren-9-yl)methoxy)carbonyl)glycyl)oxy)-4-hydroxy-1,2-diphenyl-1*H*-indole-3-carboxylate (4am). Following the general procedure, the title compound was obtain as a brown solid. (65 mg, yield = 40 %); Mp. 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.81 (s, 1H), 11.69 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 9.9 Hz, 1H), 7.48 (dd, *J* = 11.2, 9.8 Hz, 1H), 7.38 (ddd, *J* = 9.0, 8.4, 6.0 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.28 – 7.19 (m, 4H), 7.21 – 7.14 (m, 2H), 7.16 – 7.07 (m, 2H), 7.03 – 6.84 (m, 1H), 6.55 (dd, *J* = 17.2, 8.7 Hz, 1H), 5.45 (dd, *J* = 57.9, 52.7 Hz, 1H), 4.41 (dd, *J* = 9.3, 6.4 Hz, 2H), 4.25 (dd, *J* = 20.5, 13.2 Hz, 1H), 4.09 (qd, *J* = 7.1, 2.8 Hz, 2H), 3.98 (s, 1H), 0.88 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.39, 169.05, 168.38, 168.37, 156.27, 146.73, 146.55, 143.82, 142.63, 142.42, 141.24, 137.42, 137.27, 136.38, 136.29, 133.96, 132.60, 132.12, 131.43, 131.31, 130.66, 130.64, 129.45, 129.22, 129.16, 128.52, 128.48, 128.45, 128.41, 128.34, 128.33, 127.64, 127.37, 127.33, 127.06, 127.00, 125.16, 119.91, 119.53, 119.28, 116.29, 116.26, 116.07, 106.27, 106.24, 101.77, 101.53, 67.25, 61.15, 61.06, 47.09, 42.77, 41.01, 13.37; HRMS (ESI): $[M+H]^+$ calcd. for $C_{40}H_{33}N_2O_7$: 653.2282, found 653.2284.

Ethyl 5-acetoxy-1-(2-ethylphenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ba). Following the general procedure, the title compound was obtain as a white solid (66 mg, yield = 60 %); Mp. 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.37 – 7.16 (m, 9H), 7.12 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.32 (d, J = 8.7 Hz, 1H), 4.18 – 4.03 (m, 2H), 2.40 (s, 3H), 2.31 – 2.12 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.91, 168.42, 146.79, 142.54, 142.07, 137.40, 134.54, 132.50, 131.27, 130.41, 129.70, 129.39, 128.86, 128.47, 127.20, 126.44, 119.59, 116.20, 105.99, 101.75, 61.02, 23.23, 20.81, 13.90, 13.39; HRMS (EI) $[M]^+$ calcd. for $C_{27}H_{25}NO_5$: 443.1733, found 443.1737.

Ethyl 5-acetoxy-1-(4-ethylphenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ca). Following the general procedure, the title compound was obtain as an off white solid (72 mg, yield = 65 %); Mp. 155-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 7.31 – 7.23 (m, 4H), 7.23 – 7.19 (m, 2H), 7.15 (t, *J* = 5.4 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.59 (d, *J* = 8.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.74 – 2.56 (m, 2H), 2.41 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.98, 168.40, 146.70, 144.49, 142.53, 137.42, 133.86, 132.46, 131.56, 130.66, 128.53, 128.34, 128.09, 127.30, 119.48, 116.25, 106.08, 101.77, 61.01, 28.36, 20.79, 15.10, 13.37; HRMS (EI) $[M]^+$ calcd. For $C_{27}H_{25}NO_5$: 443.1733, found 443.1736.

Ethyl 5-acetoxy-4-hydroxy-1-(4-methoxyphenyl)-2-phenyl-1*H*-indole-3-carboxylate (4da). Following the general procedure, the title compound was obtain as an off white solid (88 mg, yield = 80 %); Mp. 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.32 – 7.22 (m, 4H), 7.19 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.55 (d, *J* = 8.7 Hz, 1H), 4.21 – 3.96 (m, 2H), 3.79 (s, 3H), 2.40 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.00, 168.39, 159.19, 142.56, 137.64, 132.48, 131.60, 130.64, 129.44, 129.04, 128.36, 127.36, 119.52, 116.18, 114.33, 114.29, 114.28, 106.02, 101.68, 77.31, 77.00, 76.68, 61.01, 55.39, 20.79, 13.38; HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{24}NO_6$: 446.1598, found 446.1596.

Ethyl 5-acetoxy-1-(2,4-dimethylphenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ea). Following the general procedure, the title compound was obtain as an off white solid (78 mg, yield = 71 %); Mp. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.36 – 7.17 (m, 6H), 7.03 – 6.86 (m, 4H), 6.31 (d, *J* = 8.7 Hz, 1H), 4.16 – 4.03 (m, 2H), 2.39 (s, 3H), 2.30 (s, 3H), 1.89 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.44, 168.93, 147.29, 143.07, 139.52, 137.50, 136.47, 133.09, 132.97, 132.08, 131.95, 130.81, 129.76, 128.94, 127.83, 127.74, 120.05, 116.76, 106.33, 102.19, 61.49, 21.59, 21.32, 17.97, 13.90; HRMS (EI): $[M]^+$ calcd. for $C_{27}H_{25}NO_5$: 443.1733 found 443.1731.

Ethyl 5-acetoxy-1-(3,4-dimethylphenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4fa). Following the general procedure, the title compound was obtain as an off white solid (88 mg, yield = 81 %); Mp. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.21 (m, 2H), 7.19 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.21 (s, 3H), 2.17 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.42, 168.34, 146.41, 142.66, 137.19, 136.49, 132.90, 131.53, 130.71, 129.15, 128.39, 128.37, 128.30, 127.31, 119.64, 116.31, 106.20, 101.43, 60.99, 39.09, 30.30, 27.36, 27.00, 13.39; HRMS (ESI): $[M+H]^+$ calcd. for $C_{27}H_{26}NO_5$: 444.1805 found: 444.1804.

Ethyl 5-acetoxy-1-(3,4-dimethoxyphenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ga). Following the general procedure, the title compound was obtain as a brown solid (71 mg, yield = 60 %); Mp. 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 7.36 – 7.24 (m, 3H), 7.21 (d, *J* = 6.8 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.84 – 6.75 (m, 2H), 6.70 – 6.62 (m, 1H), 6.57 (d, *J* = 2.1 Hz, 1H), 4.19 – 4.04 (m, 2H), 3.88 (s, 3H), 3.69 (s, 3H), 2.41 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.07, 168.36, 149.00, 148.69, 146.72, 142.55, 137.40, 132.45, 131.65, 130.53, 129.08, 128.42, 127.38, 120.53, 119.56, 116.16, 116.03, 111.54, 110.71, 106.00, 101.70, 61.05, 55.92, 55.89, 20.77, 13.36; HRMS (EI): $[M]^+$ calcd. for $C_{27}H_{25}NO_7$: 475.1631, found 475.1625.

Ethyl 5-acetoxy-1-(3-chlorophenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ha). Following the general procedure, the title compound was obtain as a brown solid (68 mg, yield = 61 %); Mp. 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.34 – 7.23 (m, 5H), 7.23 – 7.14 (m, 3H), 7.02 – 6.98 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 1H), 4.15 – 4.03 (m, 2H), 2.39 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.92, 168.22, 146.31, 142.72, 137.55, 137.00, 134.76, 132.73, 131.06, 130.58, 130.17, 128.72, 128.69, 128.57, 127.54, 126.66, 119.91, 116.25, 106.77, 101.34, 61.20, 20.77, 13.35; HRMS (EI): $[M]^+$ calcd. for $C_{25}H_{20}ClNO_5$: 449.1030, found 449.1033.

Ethyl 5-acetoxy-1-(4-fluorophenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ia). Following the general procedure, the title compound was obtain as a brown solid. (70 mg, yield = 65 %); Mp. 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 7.31 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 7.06 – 6.98 (m, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.7 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.96, 168.27, 161.98 (d, J_{C-F} = 247.6 Hz), 146.59, 142.69, 137.34, 132.63, 132.36, 131.28, 130.59, 130.12 (d, J_{C-F} = 8.0 Hz), 128.57, 127.49, 119.79, 116.26 (d, J_{C-F} = 22.9 Hz), 106.47, 101.37, 61.14, 20.78, 13.36; HRMS (EI): $[M]^+$ calcd. for $C_{25}H_{20}FNO_5$: 433.1326, found 433.1318.

Ethyl 5-acetoxy-4-hydroxy-2-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-indole-3-carboxylate (4ja). Following the general procedure, the title compound was obtain as an off white solid. (61 mg, yield = 51 %); Mp. 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 7.58 (dd, *J* = 17.2, 7.8 Hz, 2H), 7.36 – 7.22 (m, 5H), 7.17 (dd, *J* = 8.1, 1.4 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.91, 168.17, 146.15, 142.82, 139.65, 136.85, 132.83, 130.95, 130.60, 128.81, 128.73, 127.63, 126.41 (q, J_{C-F} = 3.6, Hz), 120.04, 116.37, 107.09, 101.19, 77.31, 76.99, 76.67, 61.27, 20.75, 13.34; HRMS (EI): $[M]^+$ calcd. for $C_{26}H_{20}F_3NO_5$: 483.1294, found 483.1286.

Ethyl 5-acetoxy-1-(2,4-dichlorophenyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ka). Following the general procedure, the title compound was obtain as a pale yellow solid (74 mg, yield = 62 %); Mp. 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.20 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.59 (d, *J* = 8.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.90, 168.12, 146.14, 142.82, 136.86, 135.79, 133.25, 132.86, 130.92, 130.87, 130.53, 130.17, 128.89, 127.72, 127.65, 120.10, 116.25, 107.08, 101.12, 61.28, 20.76, 13.33; HRMS (EI): $[M]^+$ calcd. for $C_{25}H_{19}Cl_2NO_5$: 483.0640, found 483.0639.

Ethyl 5-acetoxy-4-hydroxy-2-phenyl-1-propyl-1*H*-indole-3-carboxylate (4la). Following the general procedure, the title compound was obtain as a pale yellow solid. (76mg, yield = 80 %); Mp. 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.52 – 7.42 (m, 3H), 7.33 – 7.27 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.71 (m, 2H), 2.38 (s, 3H), 1.68 (dd, *J* = 15.2, 7.5 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.97, 168.19, 146.56, 142.76, 135.43, 132.12, 131.95, 129.92, 128.85, 127.90, 119.13, 116.59, 105.19, 100.73, 60.69, 45.99, 22.88, 20.78, 13.25, 11.23; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{24}NO_5$: 382.1649, found 382.1651.

Ethyl 5-acetoxy-1-butyl-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ma). Following the general procedure, the title compound was obtain as an off white solid. (74mg, yield = 75 %); Mp. 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1H), 7.51 – 7.40 (m, 3H), 7.32 – 7.27 (m, 2H), 7.04 – 6.97 (m, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.88 – 3.74 (m, 2H), 2.38 (s, 3H), 1.65 – 1.59 (m, 2H), 1.17 (m, 2H), 0.78 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.00, 168.20, 146.52, 142.79, 135.42, 132.13, 131.96, 129.94, 128.86, 127.91, 119.15, 116.62, 105.19, 100.71, 60.70, 44.18, 31.60, 20.80, 19.91, 13.46, 13.27; HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{26}NO_5$: 396.1805, found 396.1804.

Ethyl 5-acetoxy-1-cyclohexyl-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4na). Following the general procedure, the title compound was obtain as an off white solid. (78mg, yield = 74 %); Mp. 184-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.54 – 7.40 (m, 3H), 7.27 – 7.23 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 1H), 2.39 (s, 3H), 1.91 – 1.71 (m, 4H), 1.60 (s, 2H), 1.36 – 0.97 (m, 4H), 0.75 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.57, 168.81, 147.31, 143.40, 133.42, 132.32, 130.05, 129.34, 128.55, 119.06, 110.53, 104.08, 77.86, 77.54, 77.22, 61.20, 57.86, 31.36, 26.45, 25.67, 21.37, 13.76, 0.53; HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{28}NO_5$: 422.1962, found 422.1959.

Ethyl 5-acetoxy-1-allyl-4-hydroxy-2-phenyl-1*H*-indole 3-carboxylate (4oa). Following the general procedure, the title compound was obtain as an off white solid. (72mg, yield = 76 %); Mp. 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.57 – 7.41 (m, 1H), 7.32 (dt, *J* = 8.1, 2.1 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 5.91 – 5.71 (m, 1H), 5.17 (dd, *J* = 10.4, 0.8 Hz, 1H), 4.92 (dd, *J* = 17.2, 0.8 Hz, 1H), 4.46 (dt, *J* = 4.7, 1.7 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 1H), 2.39 (s, 1H), 0.82 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.52, 170.73, 149.21, 145.32, 138.17, 134.89, 134.65, 134.15, 132.44, 131.63, 130.45, 121.94, 120.07, 119.11, 108.04, 103.64, 63.38, 49.32, 23.38, 15.86; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{22}NO_5$: 380.1492, found 380.1494.

Ethyl 5-acetoxy-1-benzyl-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4pa). Following the general procedure, the title compound was obtain as an off white solid. (80mg, yield = 75 %); Mp. 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.53 – 7.32 (m, 3H), 7.31 – 7.11 (m, 5H), 7.05 – 6.85 (m, 3H), 6.66 (d, *J* = 8.7 Hz, 1H), 5.08 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.88, 168.16, 146.94, 142.74, 136.25, 135.81, 132.38, 131.46, 129.93, 129.02, 128.71, 127.90, 127.55, 126.02, 119.49, 116.60, 105.70, 101.31, 80.83, 60.85, 47.94, 20.78, 13.28; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{26}H_{23}NNaO_5$: 452.1468, found 452.1469.

Ethyl 5-acetoxy-1-(2,4-dichlorophenethyl)-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4qa). Following the general procedure, the title compound was obtain as an off white solid. (102 mg, yield = 80 %); Mp. 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.51 – 7.44 (m, 1H), 7.40 (dd, *J* = 11.5, 4.4 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.07 (dd, *J* = 11.3, 5.2 Hz, 4H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 4.11 (t, *J* = 7.4 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 0.78 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.20, 168.35, 146.81, 143.24, 135.42, 135.06, 133.88, 133.76,

132.64, 131.94, 131.64, 130.03, 129.68, 129.18, 128.20, 127.60, 119.78, 116.88, 105.76, 100.68, 81.10, 61.09, 59.06, 43.72, 33.32, 21.06, 13.47; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{27}H_{23}Cl_2NNaO_5$: 534.0845, found 534.0845.

Ethyl 1-(2-(1*H*-indol-3-yl)ethyl)-5-acetoxy-4-hydroxy-2-phenyl-1*H*-indole-3-carboxylate (4ra). Following the general procedure, the title compound was obtain as an off white solid. (97 mg, yield = 81 %); Mp. 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.99 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.12 – 7.07 (m, 2H), 7.04 (d, *J* = 8.7 Hz, 1H), 6.97 (t, *J* = 7.1 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 2.2 Hz, 1H), 4.25 – 4.07 (m, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.16 – 2.95 (m, 2H), 2.40 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.05, 168.22, 146.76, 142.88, 136.11, 135.30, 132.22, 131.73, 129.83, 128.73, 127.89, 126.96, 122.12, 122.07, 119.45, 119.28, 118.15, 116.66, 111.50, 111.15, 105.27, 102.90, 100.71, 77.31, 45.03, 25.53, 20.83, 13.24; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{29}H_{26}N_2NaO_5$: 505.1733, found 505.1735.

Ethyl 5-acetoxy-4-hydroxy-2-(4-methoxyphenyl)-1-phenyl-1*H*-indole-3-carboxylate (4sa). Following the general procedure, the title compound was obtain as an off white solid. (75 mg, yield = 68 %); Mp. 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 7.37 – 7.29 (m, 3H), 7.14 – 7.06 (m, 4H), 6.92 (dd, *J* = 8.7, 3.5 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.55 (d, *J* = 8.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 6.1 Hz, 3H), 2.38 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 168.47, 159.61, 146.55, 142.54, 137.24, 136.55, 132.51, 132.03, 129.21, 128.38, 128.28, 123.47, 119.44, 116.33, 112.79, 106.12, 101.58, 61.05, 55.17, 20.78, 13.60; HRMS (EI): $[M]^+$ calcd. for $C_{26}H_{24}NO_6$: 445.1525, found 445.1534.

Ethyl 5-acetoxy-1-(4-fluorophenyl)-4-hydroxy-2-(4-methoxyphenyl)-1*H*-indole-3-carboxylate (4ta). Following the general procedure, the title compound was obtain as an off white solid. (64 mg, yield = 56 %); Mp. 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.16 – 6.99 (m, 6H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.81 – 6.73 (m, 2H), 6.52 (d, *J* = 8.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.38 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.96, 168.37, 161.8 (d, J_{C-F} = 247.4 Hz), 159.68, 146.56, 142.60, 137.25, 132.56, 132.53, 132.49, 131.96, 130.11 (d, J_{C-F} = 8.7 Hz), 123.24, 119.60, 116.41, 116.29 (d, J_{C-F} = 22.7 Hz), 106.29, 101.31, 61.11, 55.18, 20.76, 13.58; HRMS (EI): $[M]^+$ calcd. for $C_{26}H_{22}NO_6$: 463.1431, found 463.1432.

Ethyl 5-acetoxy-4-hydroxy-2-methyl-1-phenyl-1*H*-indole-3-carboxylate (4ua). Following the general procedure, the title compound was obtain as an off white solid. (57 mg, yield = 65 %); Mp. 175-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 7.66 – 7.45 (m, 3H), 7.37 – 7.18 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.39 (d, *J* = 8.7 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.00, 168.90, 144.68, 142.15, 137.31, 136.18, 132.46, 129.85, 129.20, 128.26, 118.69, 101.20, 61.40, 20.78, 14.37, 13.84; HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{20}NO_5$: 354.1336, found 354.1336.

5-hydroxy-4-oxo-9-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-6-yl acetate (4va). Following the general procedure, the title compound was obtain as an off white solid. (55 mg, yield = 66 %); Mp. 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (d, *J* = 0.5 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.40 – 7.34 (m, 2H), 6.93 – 6.88 (m, 1H), 6.57 (d, *J* = 8.6 Hz, 1H), 2.78 (t, *J* = 6.2 Hz, 2H), 2.66 (dd, *J* = 7.1, 5.7 Hz, 2H), 2.38 (s, 3H), 2.28 – 2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.16, 169.82, 152.57, 142.68, 137.59, 135.64, 132.56, 129.96, 129.17, 127.04, 120.07, 115.21, 114.57, 101.45, 36.37, 23.58, 22.78, 20.77; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{20}H_{17}NNaO_4$: 358.1049, found 358.1051.

1-(3,4-dimethoxyphenyl)-4,5-dihydroxy-2-phenyl-1*H*-indole-3-carboxylic acid (5ga). A mixture of **4ga** (0.1 mmol) in 2 M NaOH (1.0 mL) was heated at 60 °C for 2 h. After completion, the reaction mixture was cooled to 0 °C and made pH to ~ 4 by adding 2N HCl. Then extracted with EtOAc and washed with water, brine, dried over sodium sulfate and evaporated under reduced pressure. The obtained crude products were purified by column chromatography to afford the pure compound as brown solid (28 mg, yield = 70 %); Mp. 191-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.37 – 7.27 (m, 5H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.83 – 6.73 (m, 2H), 6.58 (d, *J* = 8.7 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H), 3.87 (d, *J* = 4.2 Hz, 3H), 3.66 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.19, 149.07, 148.74, 148.03, 139.58, 136.25, 133.99, 130.94, 130.60, 129.05, 128.89, 127.73, 120.45, 115.35, 113.12, 111.47, 110.74, 103.01, 102.13, 55.93. HRMS (EI): $[M]^+$ calcd. for $C_{23}H_{19}NO_6$: 405.1212, found 405.1222.

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