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Domino reactions of cyclic enaminones leading to selective synthesis of pentacyclic indoles and its functionalization

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ABSTRACT

A new multicomponent domino reaction of cyclic enaminones with acenaphthylene-1,2-dione in an anhydride solvent has been established, providing selective protocol to pentacyclic indoles with different substituted patterns (up to 50 examples). Both substitutions on the cyclic enaminone ring and reaction temperatures showed obvious impact on the reaction pathways. For instance, selective allylic hydroxylation and allylic esterification of in situ generated indoles depend on reaction temperatures. With special substituents, the reactions underwent dehydrogenation process to give access to different substituted fused indoles with good to excellent yields. These reactions feature mild conditions, convenient one-pot operation and short reaction times. The purification of products only needs to be washed by 95% ethanol without traditional chromatography and recrystallization, which characterizes group-assisted purification (GAP) chemistry.

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1. Introduction

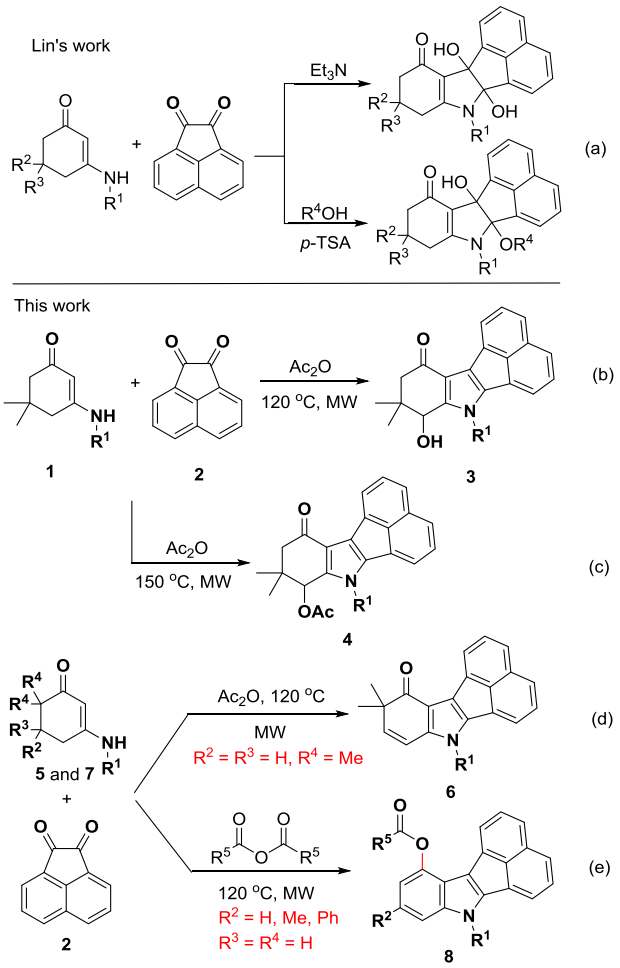
The assembly of complex polycyclic frameworks of chemical and biological interest has emerged as an active theme in modern organic chemistry.[1,2] Among these systems, the structurally diverse polycyclic indoles commonly exists in natural alkaloids[3] and often referred to as 'privileged medicinal scaffolds' in drug discovery because of their special chemical and biological activities.[4] Compounds containing this polycyclic indole moiety have been served as 3α-hydroxysteroid dehydrogenase inhibitors,[5] DNA intercalators, topoisomerase II inhibitors,[6] lipid peroxidation inhibitors,[7] and potassium channel openers.[8] Accordingly, diverse approaches to polycyclic indoles have been established.[9] However, most of these methods suffered from drawbacks including the use of transition-metal catalysts,[10] limited availability of starting materials, multistep sequences, incompatibility with various functional groups and harsh reaction conditions. Therefore, the development of reaction sequences that are short, convenient to carry out, and efficient toward complex and diverse polycyclic indoles from simple substrates continues to be of great interest in the scientific community.

Multicomponent domino reactions (MDRs) for total synthesis of natural products or natural-like structures are considered to be one of the powerful tools in the modern drug discovery and development process, enabling rapid access to structural variation and complexity within single-step conversions for the collection of polycyclic skeletons.[11] Such reactions feature bond forming efficiency and high levels of structural complexity while minimizing the generation of waste.[12] In recent years, a great deal of effort has been devoted to carrying out MDRs for the assembly of various heterocycles.[13] Over the past few years, we have also developed new multicomponent domino reactions of arylglyoxals with enaminones and different nucleophiles (Nu), providing highly substituted indoles.[14] Very recently, Shi and co-workers reported L-proline-catalyzed diastereoselective three-component reaction of acenaphthylene-1,2-dione, *N*-aryl enaminones, and barbituric acid for the synthesis of functionalized tetrahydroacenaphtho[1,2-*b*]indolones.[15] Later, Lin et al. represented a selective synthesis of acenaphtho[1,2-b]indoles with different substitution patterns using acenaphthylene-1,2-dione and *N*-aryl enaminones as starting materials. The presence of Et_3N allowed a [3+2] cyclization to yield dihydroxylated acenaphtho[1,2-b]indoles whereas the use of *p*-toluenesulfonic acid (*p*-TSA) led to alkoxylated analogue via cyclization and S_N1-type reaction with alcohols (Scheme 1a).[16] During this project, we believed that this reaction pathway may be adjusted by the use of suitable solvents or promoters to realize allylic hydroxylation of cyclic enaminones based on our previous

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studies.[14] As we had expected, this transformation was successfully accomplished under microwave heating (MW) with concomitant achievement of selective allylic hydroxylation and esterification by controlling reaction temperatures (Scheme 1b and c). Further investigations revealed that replacing 5,5-dimethylcyclohexane-1,3-dione-derived enaminones with 4,4-dimethyl counterparts allowed formal [3+2] cyclization to deliver pentacyclic-fused indoles **6** through dehydrogenation (Scheme 1d). Besides, monosubstituent such as a methyl or a phenyl group at 5-postion of cyclic enaminones was proven to be an effective substrate, transforming into the aromatic pentacyclic-fused indoles **8** through esterification (Scheme 1e). Notably, purification of these pentacyclic-fused indoles could be achieved without traditional chromatography or recrystallization. Instead, products were isolated by diluting the reaction mixture with common solvents such as water or ethanol, and then collecting the precipitated solids by filtration. Such purifications characterize group-assisted purification (GAP) chemistry.[17] In this paper, we report these interesting observations.

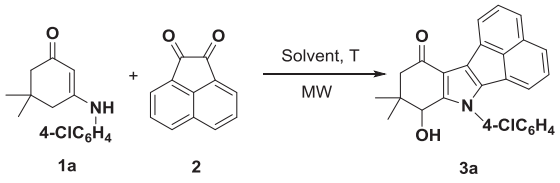


Scheme 1. Selective synthesis of pentacyclic indoles.

2. Results and discussion

Initially, we performed the reaction of 3-((4-chlorophenyl) amino)-5,5-dimethylcyclohex-2-enone (**1a**) with acenaphthylene-1,2-dione (**2**) in HOAc under microwave (MW) irradiation to evaluate the feasibility of allylic hydroxylation. The desired allylic hydroxylated product **3a** was obtained, albeit with very low yield (15%, Table 1, entry 1). Subsequently, the reaction conditions were optimized to improve the yield of **3a**. The solvent effect was first investigated, and different solvents often used in organic synthesis, such as THF, MeCN, 1,4-dioxane, TFA and DMF, were employed. Disappointedly, all these solvents failed to give the desired product **3a** at 100 °C under microwave irradiation (entries 2–6). Considering the dehydration in cyclization process, we decided to use Ac_2O as both a dehydrating agent and a solvent to improve the reaction efficiency. The formal [3+2] cyclization in Ac_2O[18] worked efficiently to give product **3a** with an isolated yield of 46% (entry 7). Next, we observed that the increase of the reaction temperature facilitated the reaction process. Elevating temperature to 110 °C led to a 65% yield (entry 8). The best result (78%) was achieved when the temperature was enhanced to 120 °C (entry 9). Further increasing the reaction temperature is beneficial to form esterification product **4a**. After careful optimizations, we found that the reaction at 120 °C preferred to give the allylic hydroxylated product **3a** whereas allylic esterification product **4a** was obtained in 81% chemical yield as the reaction was carried out at 150 °C.

Table 1
Optimization conditions for forming **3a**[a]



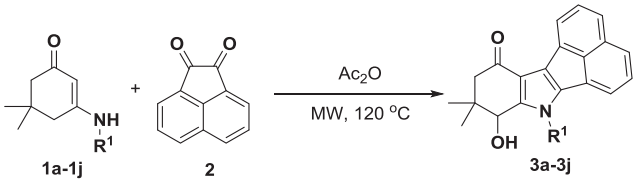
Entry	Solvent	T/°C	Time/min	Yield[b]/%
1	HOAc	100	22	15
2	THF	100	22	Trace
3	MeCN	100	22	Trace
4	1,4-Dioxane	100	22	Trace
5	TFA	100	22	Trace
6	DMF	100	22	Trace
7	Ac_2O	100	22	46
8	Ac_2O	110	22	65
9	Ac_2O	120	22	78
10	Ac_2O	130	22	56
11	Ac_2O	150	22	Trace

[a] Reaction conditions: 3-((4-chlorophenyl)amino)-5,5-dimethylcyclo hex-2-enone (**1a**, 1.0 mmol), acenaphthylene-1,2-dione (**2**, 1.0 mmol), solvent (2.0 mL), microwave irradiation.
[b] Isolated yield.

With the optimized conditions in hand, we then used various preformed N-substituted enaminones to explore the scope of allylic hydroxylation and esterification, respectively. The results are presented in Tables 2 and 3. Upon repeating the reaction with acenaphthylene-1,2-dione (**2**) at 120 °C, we are pleased to find that the formal [3+2] cyclization reaction tolerated a broad spectrum of enaminones **1a**–**1j** bearing both electron-donating and electron-withdrawing groups, efficiently transformed into the corresponding poly-functionalized pentacyclic-fused indoles **3a**–**3j** with yields ranging from 72% to 85%. The variant of substituents that resided at different positions on the phenyl ring, such as fluoro, chloro, bromo, methyl, and methoxy, was compatible (Table 2). After the successful realization of allylic hydroxylation, we next extended our investigation to the allylic esterification by adjusting reaction temperature to 150 °C under microwave heating. As per our expectation, a series of new esterified pentacyclic-fused indoles **4a**–**4o** with 64%–81% yields were provided in a highly selective and functional group-compatible manner under the optimized conditions.

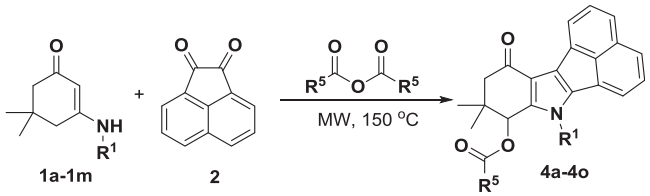
Various anhydrides, such as acetic anhydride, propionic anhydride, butyric anhydride and isobutyric anhydride could be served

Table 2
Domino synthesis of pentacyclic indoles **3**



Entry	3	R^1 (1)	Time/min	Yield/%
1	**3a**	4-ClC_6H_4 (**1a**)	22	78
2	**3b**	4-FC_6H_4 (**1b**)	23	75
3	**3c**	3,4-$Cl_2C_6H_3$ (**1c**)	18	74
4	**3d**	3,5-$Cl_2C_6H_3$ (**1d**)	24	74
5	**3e**	4-BrC_6H_4 (**1e**)	26	77
6	**3f**	3-Br-4-MeC_6H_3 (**1f**)	22	75
7	**3g**	C_6H_5 (**1g**)	20	72
8	**3h**	4-MeC_6H_4 (**1h**)	23	82
9	**3i**	3-MeC_6H_4 (**1i**)	28	70
10	**3j**	4-$MeOC_6H_4$ (**1j**)	25	85

Table 3
Domino synthesis of pentacyclic indoles **4**



Entry	4	R^1 (1)	R^5	Time/min	Yield/%
1	**4a**	4-ClC_6H_4 (**1a**)	Me	20	81
2	**4b**	4-$O_2NC_6H_4$ (**1k**)	Me	29	66
3	**4c**	2-MeC_6H_4 (**1l**)	Me	28	67
4	**4d**	4-FC_6H_4 (**1b**)	Et	23	70
5	**4e**	3,4-$Cl_2C_6H_3$ (**1c**)	Et	22	78
6	**4f**	3,5-$Cl_2C_6H_3$ (**1d**)	Et	25	71
7	**4g**	4-BrC_6H_4 (**1e**)	Et	17	74
8	**4h**	4-$O_2NC_6H_4$ (**1k**)	Et	26	69
9	**4i**	C_6H_5 (**1g**)	Et	22	72
10	**4j**	3-MeC_6H_4 (**1i**)	Et	28	70
11	**4k**	2-MeC_6H_4 (**1l**)	Et	30	64
12	**4l**	4-$MeOC_6H_4$ (**1j**)	Et	19	77
13	**4m**	4-BrBn (**1m**)	Et	26	71
14	**4n**	C_6H_5 (**1g**)	*n*-Pr	25	72
15	**4o**	4-$MeOC_6H_4$ (**1j**)	*i*-Pr	28	68

as dehydration reagents, esterification reagents, and reaction as well as media Bronsted acid promoter for the allylic functionalization simultaneously. Different electronic nature of substituents enaminones **1** did not hamper the reaction process. A range of enaminones **1a**–**1m** possessing either electron-deficient, electron-neutral, or electron-rich substituents at different positions on the aromatic ring were well-tolerated. Notably, the sterically more demanding *ortho*-substituted *N*-aryl enaminone **1l** was found to have no influence on the course of the reaction, with esterification product **4c** afforded in 67% yield. Alternatively, *N*-benzyl enaminone **1m** can show high reactivity, generating the corresponding product **4m** in 71% yield. Indeed, this protocol enabled the direct formations of C–O bonds from allylic C–H bonds without the use of any metal catalysts, giving new examples for selective synthesis of fused indoles with different substituted patterns in a step-economical fashion, depending on different reaction temperatures. The unequivocally structural elucidation was determined by their NMR spectroscopic analysis. In cases of **3j** and **4f**, their structures were further confirmed by X-ray diffraction analysis (Figs. 1 and 2).

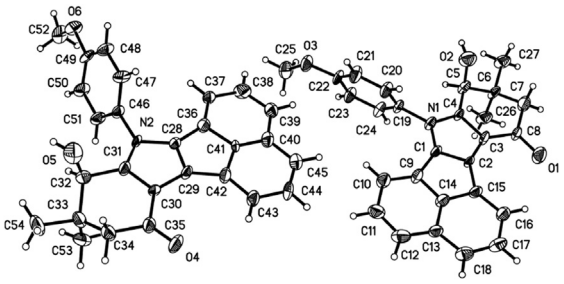


Fig. 1. X-ray structure of **3j**.[19]

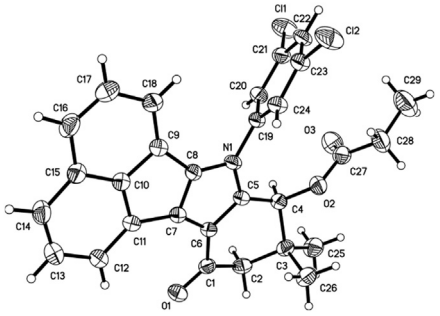
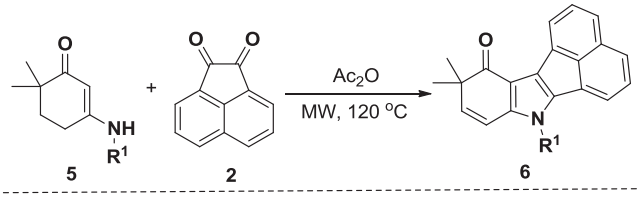


Fig. 2. X-ray structure of **4f**.[20]

After successful formation of fused indoles **3** and **4**, we turned our attention to investigating several differently substituted *N*-aryl enaminones to expand the synthetic utility of this methodology. We set out to use 6,6-dimethyl substituted enaminones **5** to replace 5,5-dimethyl analogue. The reaction was conducted at 120 °C under microwave heating, and 7-hydroxy fused indoles **4** were not obtained. Instead, dehydrogenated fused indoles **6** were afforded in good to excellent yields of 68%–85%. 4,4-Dimethyl substituted enaminones **5** carrying either electronically neutral, rich, or poor groups could be successfully engaged in the transformation (Scheme 2). Among them, halogen-containing enaminones **5** could be utilized and well-tolerated under the optimal conditions, delivering the expected products in good yields, which provide possible potential for further functionalizations by modern cross-coupling reactions. The structure of **6d** was determined by X-ray diffraction analysis (Fig. 3).



Scheme 2. Domino synthesis of pentacyclic indoles **6**.

On the basis of these observations described above, we believed that flexible structural modification of fused indole skeleton could be achieved by selectively introducing substituents at different positions of cyclic enaminone ring. Replacing 6,6-dimethyl substituted enaminones **5** with 5-mono-substituted counterparts

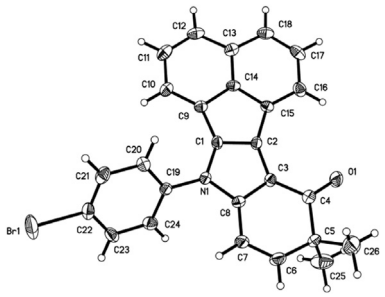
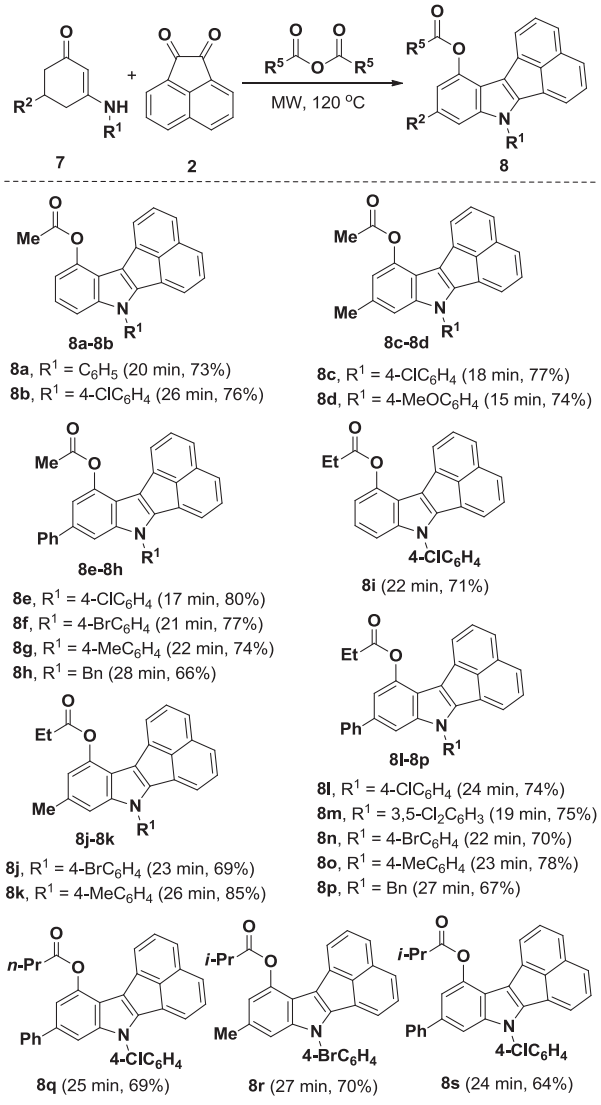


Fig. 3. X-ray structure of **6d**.[21]

7 further probed the reaction scope. The reaction proceeded smoothly to give access to a series of unprecedented pentacyclic indoles **8** in good yields through domino dehydrogenation, aromatization, and esterification sequence under the optimal conditions described above. The results exhibit the wide scope and generality of this new multicomponent domino reaction with respect to various N-substituted enaminones with different electronic properties and anhydrides like acetic, propionic, butyric, and isobutyric anhydrides (Scheme 3). The variation of substituents on cyclohexenone ring including methyl and phenyl groups all worked well for the present cyclization reaction and effectively converted into functionalized pentacyclic indoles **8**. In addition to *N*-aryl substituents, *N*-benzyl enaminone was also found to be a suitable substrate, affording the corresponding functionalized esterification products **8h** and **8p** in 66% and 67% yields, respectively. The structure of product **8e** was based on X-ray diffraction analysis (Fig. 4).



Scheme 3. Domino synthesis of pentacyclic indoles **8**.

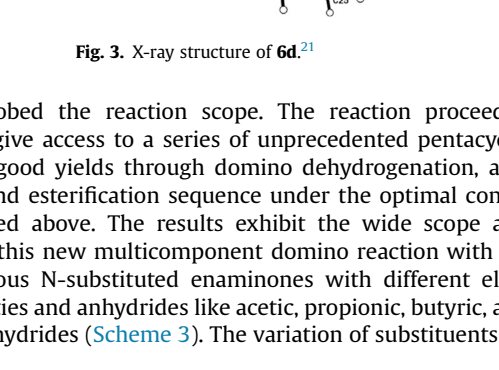
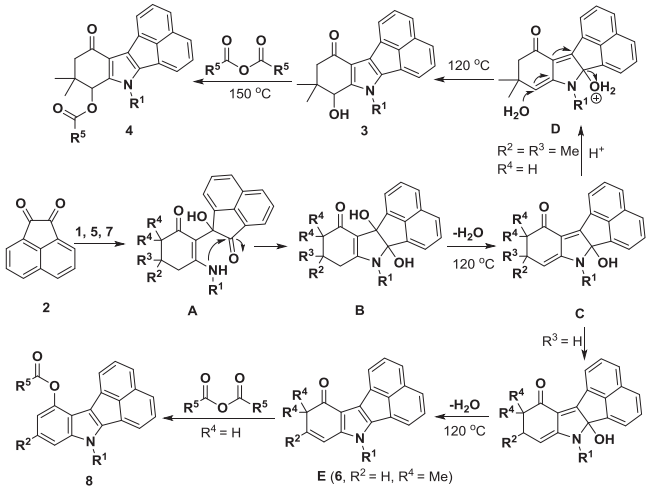


Fig. 4. X-ray structure of **8e**.[22]

On the basis of the above observations and report survey,[15,16] reasonable mechanisms for the selective formation of products **3**, **4**, **6**, and **8** are proposed as shown in Scheme 4. The initial nucleophilic addition of enaminone **1**, **5**, and **7** to acenaphthylene-1,2-dione **2** generates intermediates **A**, followed by intramolecular cyclization and dehydration to gives intermediates **C**. With two methyl groups (R^2=R^3=Me) occupying C5-position of cyclohexenone ring, intermediates **C** undergo protonation of hydroxy group and subsequent nucleophilic addition with water molecules, produce allylic hydroxylated fused indoles **3**. At higher reaction temperature, products **3** are further transformed into fused indoles **4** through esterification with anhydrides. Similar to the former, when R^3 is hydrogen and R^4 is a methyl group, intermediates **C** undergo second dehydration to yield products **6** whereas the esterification indoles **7** are afforded through successive dehydration of intermediate **C** and esterification of intermediate **E** with both R^3 and R^4 being hydrogen.



Scheme 4. Proposed mechanism for forming **3**, **4**, **6**, and **8**.

3. Conclusion

In conclusion, we have described a new and practical multi-component domino reactions (N substituted enaminones and acenaphthylene-1,2-dione) for selective synthesis of a broad range of new pentacyclic indoles with various functionalizations including allylic hydroxylation and esterification, depending on reaction temperatures and substituted patterns on cyclohexenone ring. These reactions feature convenient one-pot operation, short reaction times and flexible modification of fused indole skeleton. Additionally, the pure products could be obtained by using group-assisted purification (GAP) chemistry/technology, avoiding traditional chromatography and recrystallization purification. The biological evaluation of the resulting pentacyclic indoles is underway in our lab.

4. Experimental section

Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FTIR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 with chemical shift (δ) given in ppm relative to TMS as internal standard [(s=singlet, d=doublet, t=triplet, br s=broad singlet, m=multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

4.1. General procedure for the synthesis of compounds 3a–3j

*4.1.1. 7-(4-Chlorophenyl)-8-hydroxy-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3a**).* In a typical experiment procedure, 3-((4-chlorophenyl)amino)-5,5-dimethylcyclohex-2-enone **1a** (1.0 mmol, 0.249 g, 1.0 equiv) and acenaphthylene-1,2-dione **2** (1.0 mmol, 0.182 g, 1.0 equiv) were introduced in a 10-mL Initiator™ reaction vial, acetic anhydride (1.5 mL) was then successively added. Subsequently, the reaction vial was capped and then pre-stirring for 20 s. The mixture was irradiated (Time: 22 min, Temperature: 120 °C; Absorption Level: High; Fixed Hold Time) until TLC revealed that conversion of the starting materials were completed. The reaction mixture was then cooled to room temperature and then diluted with cold water (25 mL). The solid product was collected by Büchner filtration to give almost pure allylic hydroxylated indoles **3a**, which was further purified by washing from 95% ethanol.

A yellow solid: 0.322 g, yield 78%; mp: 226–228 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, J=6.8 Hz, ArH), 7.91 (d, 2H, J=8.8 Hz, ArH), 7.80 (t, 4H, J=7.6 Hz, ArH), 7.62 (t, 1H, J=7.2 Hz, ArH), 7.46 (t, 1H, J=7.6 Hz, ArH), 7.20 (d, 1H, J=7.2 Hz, ArH), 5.68 (d, 1H, J=7.6 Hz, CH), 4.13 (d, 1H, J=8.0 Hz, OH), 2.86 (d, 1H, J=16.4 Hz, CH), 2.16 (d, 1H, J=16.4 Hz, CH), 1.11 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 147.9, 139.4, 136.1, 133.9, 131.7, 130.5, 129.5, 128.6, 128.5, 128.2, 127.9, 127.2, 126.9, 125.0, 123.6, 120.0, 116.1, 68.3, 47.4, 26.1, 26.0; IR (KBr, ν, cm^{-1}): 3442, 3068, 1678, 1647, 1523, 1496, 1456, 1432, 1403, 1381, 1347; HRMS (ESI): m/z calcd for: $C_{26}H_{19}ClNO_2$, 412.1105 $[M-H]^-$; found: 412.1116.

*4.1.2. 7-(4-Fluorophenyl)-8-hydroxy-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3b**).* A yellow solid: 0.298 g, yield 75%; mp: 215–217 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.03 (d, 1H, J=6.8 Hz, ArH), 7.92–7.89 (m, 2H, ArH), 7.79 (d, 2H, J=8.4 Hz, ArH), 7.63–7.60 (m, 1H, ArH), 7.55 (t, 2H, J=8.8 Hz, ArH), 7.45 (t, 1H, J=7.2 Hz, ArH), 7.14 (d, 1H, J=6.8 Hz, ArH), 5.64 (d, 1H, J=7.6 Hz, CH), 4.10 (d, 1H, J=7.6 Hz, OH), 2.86 (d, 1H, J=16.4 Hz, CH), 2.15 (d, 1H, J=16.4 Hz, CH), 1.10 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 162.4 ($^1J_{CF}$=244.5 Hz), 148.0, 139.6, 133.5 ($^4J_{CF}$=2.8 Hz), 131.8 ($^3J_{CF}$=7.7 Hz), 129.5, 128.7, 128.6(3), 128.6(1), 128.5(8), 127.8, 127.2, 126.8, 124.8, 123.5, 119.9, 117.3 ($^2J_{CF}$=22.8 Hz), 115.9, 68.3, 47.4, 26.2, 26.0; IR (KBr, ν, cm^{-1}): 3431, 3083, 1726, 1650, 1608, 1513, 1481, 1458, 1427, 1402, 1347, 1320; HRMS (ESI): m/z calcd for: $C_{26}H_{19}FNO_2$, 396.1400 $[M-H]^-$; found: 396.1412.

*4.1.3. 7-(3,4-Dichlorophenyl)-8-hydroxy-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3c**).* A yellow solid: 0.331 g, yield 74%; mp: 168–170 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.24 (s, 1H, ArH), 8.04 (d, 1H, J=6.8 Hz, ArH), 7.99 (d, 1H, J=8.4 Hz, ArH), 7.91 (d, 1H, J=7.2 Hz, ArH), 7.82 (d, 2H, J=8.0 Hz, ArH), 7.63 (t, 1H, J=7.6 Hz, ArH), 7.48 (t, 1H, J=7.2 Hz, ArH), 7.24 (d, 1H, J=6.8 Hz, ArH), 5.72 (d, 1H, J=7.6 Hz, CH), 4.19 (d, 1H, J=7.6 Hz, OH), 2.84 (d, 1H, J=16.8 Hz, CH), 2.18 (d, 1H, J=16.0 Hz, CH), 1.11 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.8, 147.9, 139.3, 137.1, 132.7, 132.3, 132.2, 131.7, 131.6, 129.5, 128.6, 128.4, 128.3, 127.9, 127.3, 127.0, 126.8, 125.2, 123.7, 120.1, 116.3, 68.3, 47.5, 26.0, 25.9; IR (KBr, ν, cm^{-1}): 3420, 3071, 1750, 1726, 1651, 1606, 1594, 1525, 1480, 1458, 1429, 1349, 1317; HRMS (ESI): m/z calcd for: $C_{26}H_{18}Cl_2NO_2$, 446.0715 $[M-H]^-$; found: 446.0704.

*4.1.4. 7-(3,5-Dichlorophenyl)-8-hydroxy-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3d**).* A yellow solid: 0.331 g, yield 74%; mp: 250–252 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.06–8.03 (m, 3H, ArH), 7.93 (s, 1H, ArH), 7.82 (d, 2H, J=8.0 Hz, ArH), 7.63 (t, 1H, J=7.2 Hz, ArH), 7.49 (t, 1H, J=7.6 Hz, ArH), 7.22 (d, 1H, J=7.2 Hz, ArH), 5.75 (d, 1H, J=7.6 Hz, CH), 4.21 (d, 1H, J=7.6 Hz, OH), 2.84 (d, 1H, J=16.4 Hz, CH), 2.20 (d, 1H, J=16.4 Hz, CH), 1.12 (s, 3H, CH_3), 1.00 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.8, 147.9, 139.5, 139.3, 135.5, 131.7, 131.6, 129.5, 129.3, 128.6, 128.4, 127.9, 127.4, 127.0, 125.4, 125.3, 123.8, 119.9, 116.4, 68.4, 47.6, 26.1, 25.8; IR (KBr, ν, cm^{-1}): 3436, 3080, 1722, 1655, 1608, 1587, 1572, 1526, 1480, 1459, 1434, 1387, 1348; HRMS (ESI): m/z calcd for: $C_{26}H_{18}Cl_2NO_2$, 446.0715 $[M-H]^-$; found: 446.0707.

*4.1.5. 7-(4-Bromophenyl)-8-hydroxy-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3e**).* A yellow solid: 0.352 g, yield 77%; mp: 224–225 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, J=6.8 Hz, ArH), 7.92 (d, 2H, J=8.8 Hz, ArH), 7.85–7.80 (m, 4H, ArH), 7.62 (t, 1H, J=7.2 Hz, ArH), 7.46 (t, 1H, J=7.2 Hz, ArH), 7.21 (d, 1H, J=7.2 Hz, ArH), 5.67 (d, 1H, J=7.6 Hz, CH), 4.13 (d, 1H, J=7.6 Hz, OH), 2.86 (d, 1H, J=16.4 Hz, CH), 2.16 (d, 1H, J=16.4 Hz, CH), 1.11 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 147.9, 139.3, 136.5, 133.4, 131.7, 129.5, 128.6, 128.5, 128.4, 127.9, 127.3, 126.9, 125.1, 123.6, 122.4, 120.1, 116.1, 68.3, 47.4, 26.1, 26.0; IR (KBr, ν, cm^{-1}): 3445, 3068, 1648, 1524, 1495, 1456, 1431, 1418, 1402, 1379, 1366, 1346; HRMS (ESI): m/z calcd for: $C_{26}H_{19}BrNO_2$, 456.0599 $[M-H]^-$; found: 456.0608.

*4.1.6. 7-(3-Bromo-4-methylphenyl)-8-hydroxy-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3f**).* A yellow solid: 0.353 g, yield 75%; mp: 214–216 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.12 (s, 1H, ArH), 8.03 (d, 1H, J=6.8 Hz, ArH), 7.81 (d, 3H, J=8.4 Hz, ArH), 7.70 (d, 1H, J=8.0 Hz, ArH), 7.62 (t, 1H, J=7.6 Hz, ArH), 7.47 (t, 1H, J=7.6 Hz, ArH), 7.17 (d, 1H, J=7.2 Hz, ArH), 5.67 (d, 1H, J=7.6 Hz, CH), 4.12 (d, 1H, J=7.6 Hz, OH), 2.86 (d, 1H, J=16.8 Hz, CH), 2.52 (s, 3H, CH_3), 2.15 (d, 1H, J=16.4 Hz, CH), 1.11 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 147.9, 139.4, 138.9, 136.1, 132.6, 131.7, 129.5(4), 129.5(1), 128.6(3), 128.5(7), 127.9, 127.2, 126.9, 125.6, 125.0, 124.9, 123.6, 119.8, 116.0, 68.4, 47.4, 26.1, 26.0, 22.7; IR (KBr, ν, cm^{-1}): 3351, 3044, 1656, 1639,

1603, 1570, 1521, 1498, 1478, 1456, 1404, 1366, 1347; HRMS (ESI): *m*/*z* calcd for: $C_{27}H_{21}BrNO_2$, 470.0756 $[M-H]^-$; found: 470.0767.

*4.1.7. 8-Hydroxy-9,9-dimethyl-7-phenyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3g**).* A yellow solid: 0.273 g, yield 72%; mp: 195–197 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, *J*=6.8 Hz, ArH), 7.86 (d, 2H, *J*=7.2 Hz, ArH), 7.80 (d, 2H, *J*=8.0 Hz, ArH), 7.72 (t, 2H, *J*=7.6 Hz, ArH), 7.66–7.60 (m, 2H, ArH), 7.44 (t, 1H, *J*=7.6 Hz, ArH), 7.14 (d, 1H, *J*=7.2 Hz, ArH), 5.65 (d, 1H, *J*=7.6 Hz, CH), 4.11 (d, 1H, *J*=7.6 Hz, OH), 2.88 (d, 1H, *J*=16.4 Hz, CH), 2.15 (d, 1H, *J*=16.4 Hz, CH), 1.11 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 148.0, 139.5, 137.2, 131.9, 131.8, 130.4, 129.6, 129.5, 128.8, 128.6, 127.8, 127.1, 126.7, 126.3, 124.9, 123.5, 119.8, 116.0, 68.4, 47.3, 26.3, 26.0; IR (KBr, ν, cm^{-1}): 3432, 3043, 1715, 1638, 1594, 1518, 1458, 1397, 1362, 1348; HRMS (ESI): *m*/*z* calcd for: $C_{26}H_{20}NO_2$, 378.1494 $[M-H]^-$; found: 378.1482.

*4.1.8. 8-Hydroxy-9,9-dimethyl-7-(p-tolyl)-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3h**).* A yellow solid: 0.322 g, yield 82%; mp: 194–196 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.03 (d, 1H, *J*=6.8 Hz, ArH), 7.80–7.77 (m, 2H, ArH), 7.73 (d, 2H, *J*=8.0 Hz, ArH), 7.63–7.59 (m, 1H, ArH), 7.51 (d, 2H, *J*=8.4 Hz, ArH), 7.46–7.42 (m, 1H, ArH), 7.14 (d, 1H, *J*=6.8 Hz, ArH), 5.61 (d, 1H, *J*=7.6 Hz, CH), 4.09 (d, 1H, *J*=7.6 Hz, OH), 2.87 (d, 1H, *J*=16.4 Hz, CH), 2.48 (s, 3H, CH_3), 2.13 (d, 1H, *J*=16.8 Hz, CH), 1.11 (s, 3H, CH_3), 0.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 148.0, 139.5, 139.1, 134.6, 131.9, 131.8, 130.8, 129.5, 128.8, 128.6, 127.8, 127.1, 126.7, 126.1, 124.7, 123.4, 119.8, 115.8, 68.4, 47.3, 26.3, 25.9, 21.3; IR (KBr, ν, cm^{-1}): 3441, 3067, 1648, 1607, 1516, 1482, 1456, 1433, 1390, 1380, 1366, 1346; HRMS (ESI): *m*/*z* calcd for: $C_{27}H_{22}NO_2$, 392.1651 $[M-H]^-$; found: 392.1665.

*4.1.9. 8-Hydroxy-9,9-dimethyl-7-(m-tolyl)-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3i**).* A yellow solid: 0.275 g, yield 70%; mp: 165–167 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.03 (d, 1H, *J*=6.8 Hz, ArH), 7.80–7.78 (m, 2H, ArH), 7.67–7.57 (m, 4H, ArH), 7.44 (t, 2H, *J*=7.6 Hz, ArH), 7.14 (d, 1H, *J*=6.8 Hz, ArH), 5.64 (d, 1H, *J*=7.6 Hz, CH), 4.11 (d, 1H, *J*=7.6 Hz, OH), 2.87 (d, 1H, *J*=16.4 Hz, CH), 2.49 (s, 3H, CH_3), 2.14 (d, 1H, *J*=16.4 Hz, CH), 1.11 (s, 3H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 147.9, 140.1, 139.4, 137.1, 131.9, 131.8, 130.2, 130.1, 129.5, 128.8, 128.6, 127.8, 127.1, 126.7, 126.6, 124.8, 123.4, 123.3, 119.9, 115.9, 68.3, 47.3, 26.3, 25.9, 21.4; IR (KBr, ν, cm^{-1}): 3433, 3043, 1653, 1609, 1591, 1523, 1493, 1478, 1456, 1398, 1376, 1346; HRMS (ESI): *m*/*z* calcd for: $C_{27}H_{22}NO_2$, 392.1651 $[M-H]^-$; found: 392.1662.

*4.1.10. 8-Hydroxy-7-(4-methoxyphenyl)-9,9-dimethyl-9,10-dihydro-7H-acenaphtho[1,2-b]indol-11(8H)-one (**3j**).* A yellow solid: 0.348 g, yield 85%; mp: 259–261 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.02 (d, 1H, *J*=6.8 Hz, ArH), 7.77 (t, 4H, *J*=8.4 Hz, ArH), 7.63–7.59 (m, 1H, ArH), 7.44 (t, 1H, *J*=7.2 Hz, ArH), 7.24 (d, 2H, *J*=9.2 Hz, ArH), 7.13 (d, 1H, *J*=6.8 Hz, ArH), 5.60 (d, 1H, *J*=7.6 Hz, CH), 4.07 (d, 1H, *J*=7.6 Hz, OH), 3.91 (s, 3H, OCH_3), 2.87 (d, 1H, *J*=16.4 Hz, CH), 2.13 (d, 1H, *J*=16.8 Hz, CH), 1.11 (s, 3H, CH_3), 0.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 159.9, 148.1, 139.7, 132.0, 131.8, 129.8, 129.5, 128.8, 128.6, 127.8, 127.7, 127.0, 126.6, 124.5, 123.4, 119.8, 115.7, 115.4, 68.3, 56.0, 47.3, 26.3, 25.9; IR (KBr, ν, cm^{-1}): 3336, 3055, 1644, 1612, 1513, 1459, 1438, 1380, 1346; HRMS (ESI): *m*/*z* calcd for: $C_{27}H_{22}NO_3$, 408.1600 $[M-H]^-$; found: 408.1591.

4.2. General procedure for the synthesis of 4a–4o

*4.2.1. 7-(4-Chlorophenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl acetate (**4a**).* In a typical experiment procedure, 3-((4-chlorophenyl)amino)-5,5-dimethylcyclohex-2-enone **1a** (1.0 mmol, 0.249 g, 1.0 equiv) and acenaphthylene-1,2-dione **2** (1.0 mmol, 0.182 g, 1.0 equiv) were introduced in a 10-mL Initiator™ reaction vial, acetic anhydride (1.5 mL) was then successively added. Subsequently, the reaction vial was capped and then pre-stirring for 20 s. The mixture was irradiated (Time: 20 min, Temperature: 150 °C; Absorption Level: High; Fixed Hold Time) until TLC revealed that conversion of the starting materials were completed. The reaction mixture was then cooled to room temperature and then diluted with cold water (25 mL). The solid product was collected by Büchner filtration to give almost pure allylic esterified indoles **4a**, which was further purified by washing from 95% ethanol.

A yellow solid: 0.369 g, yield 81%; mp: 205–207 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.05 (d, 1H, *J*=6.4 Hz, ArH), 7.83 (d, 2H, *J*=8.0 Hz, ArH), 7.75 (d, 2H, *J*=8.4 Hz, ArH), 7.70 (d, 2H, *J*=8.0 Hz, ArH), 7.64 (t, 1H, *J*=7.6 Hz, ArH), 7.45 (t, 1H, *J*=7.2 Hz, ArH), 7.04 (d, 1H, *J*=6.8 Hz, ArH), 5.85 (s, 1H, CH), 2.74 (d, 1H, *J*=16.8 Hz, CH), 2.39 (d, 1H, *J*=16.4 Hz, CH), 1.91 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 169.8, 142.6, 140.8, 135.6, 134.6, 131.7, 131.4, 130.6, 129.6, 128.9, 128.7, 128.0, 127.9, 127.6, 127.0, 124.5, 123.7, 120.1, 117.5, 69.4, 48.4, 26.1, 25.0, 20.7; IR (KBr, ν, cm^{-1}): 3057, 1754, 1688, 1568, 1514, 1522, 1490, 1387, 1359, 1320; HRMS (ESI): *m*/*z* calcd for: $C_{28}H_{22}ClNNaO_3$, 478.1186 $[M+Na]^+$; found: 478.1197.

*4.2.2. 9,9-Dimethyl-7-(4-nitrophenyl)-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl acetate (**4b**).* A yellow solid: 0.308 g, yield 66%; mp: 220–222 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.52 (d, 2H, *J*=8.8 Hz, ArH), 8.08 (d, 1H, *J*=6.8 Hz, ArH), 8.00 (d, 2H, *J*=8.8 Hz, ArH), 7.85 (d, 2H, *J*=8.4 Hz, ArH), 7.66 (t, 1H, *J*=6.8 Hz, ArH), 7.45 (t, 1H, *J*=7.6 Hz, ArH), 7.15 (d, 1H, *J*=7.2 Hz, ArH), 5.92 (s, 1H, CH), 2.76 (d, 1H, *J*=16.4 Hz, CH), 2.43 (d, 1H, *J*=16.8 Hz, CH), 1.88 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.03 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.9, 169.9, 148.1, 142.5, 142.2, 140.5, 131.7, 131.2, 129.6, 128.7, 128.4, 127.9, 127.8, 127.3, 127.2, 126.0, 125.0, 124.0, 120.5, 118.0, 69.5, 48.4, 26.1, 24.9, 20.6; IR (KBr, ν, cm^{-1}): 3069, 1754, 1693, 1608, 1573, 1521, 1481, 1388, 1351, 1348; HRMS (ESI): *m*/*z* calcd for: $C_{28}H_{22}N_2NaO_5$, 489.1426 $[M+Na]^+$; found: 489.1411.

*4.2.3. 9,9-Dimethyl-11-oxo-7-(o-tolyl)-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl acetate (**4c**).* A yellow solid: 0.291 g, yield 67%; mp: 165–167 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, *J*=7.2 Hz, ArH), 7.81–7.77 (m, 2H, ArH), 7.65–7.61 (m, 1H, ArH), 7.57–7.54 (m, 2H, ArH), 7.48–7.45 (m, 2H, ArH), 7.40–7.36 (m, 1H, ArH), 6.69 (d, 1H, *J*=7.2 Hz, ArH), 5.85+5.56 (s, 1H, CH), 2.79–2.67 (m, 1H, CH), 2.47–2.35 (m, 1H, CH), 2.06 (d, 3H, *J*=6.0 Hz, CH_3), 1.94+1.75 (s, 3H, CH_3), 1.12 (d, 3H, *J*=6.8 Hz, CH_3), 1.00 (d, 3H, *J*=5.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.7(1), 192.6(6), 169.6, 169.3, 142.5, 142.4, 140.9, 140.7, 135.8, 135.5, 135.2, 132.0, 131.8, 131.7(2), 131.6(8), 130.6, 130.5, 129.6, 129.5, 128.7, 128.2(5), 128.1(8), 128.1, 128.0(3), 127.9(9), 127.9(5), 127.9(1), 127.8, 127.4(3), 127.4(0), 126.8(3), 126.8(1), 124.1(2), 124.0(7), 123.6, 119.3, 119.1, 117.1, 117.0, 69.5, 69.4, 48.9, 48.3, 26.3, 26.0, 24.9, 24.4, 20.8, 20.2, 17.2, 17.1; IR (KBr, ν, cm^{-1}): 3033, 1764, 1698, 1656, 1580, 1478, 1425, 1398, 1366, 1347; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{25}NNaO_3$, 458.1732 $[M+Na]^+$; found: 458.1749.

*4.2.4. 7-(4-Fluorophenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4d**).* A yellow solid: 0.317 g, yield 70%; mp: 189–191 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, *J*=6.8 Hz, ArH), 7.82 (d, 2H, *J*=8.0 Hz, ArH), 7.72 (s, 2H, ArH), 7.64 (t, 1H, *J*=7.2 Hz, ArH), 7.51 (t, 2H, *J*=8.0 Hz, ArH), 7.43 (t, 1H, *J*=7.2 Hz, ArH), 6.99 (d, 1H, *J*=6.8 Hz, ArH), 5.90 (s, 1H, CH), 2.72 (d, 1H, *J*=16.4 Hz, CH), 2.40 (d, 1H, *J*=16.4 Hz, CH), 2.30–2.21 (m, 1H, CH), 2.16–2.06 (m, 1H, CH), 1.14 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.92 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 173.0, 162.7 ($^1J_{CF}$=245.5 Hz), 142.7, 141.0, 133.1,

131.7 ($^{2}J_{CF}$=25.5 Hz), 129.6, 129.4, 129.3 ($^{4}J_{CF}$=2.6 Hz), 128.6, 128.1, 127.8, 127.5, 126.9, 124.3, 123.7, 119.9, 117.6, 117.4 ($^{3}J_{CF}$=5.7 Hz), 69.3, 48.5, 27.0, 26.2, 24.9, 9.4; IR (KBr, ν, cm^{-1}): 3059, 1735, 1660, 1614, 1511, 1480, 1459, 1416, 1390, 1370, 1361; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{24}FNNaO_3$, 476.1638 $[M+Na]^+$; found: 476.1625.

*4.2.5. 7-(3,4-Dichlorophenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4e**).* A yellow solid: 0.392 g, yield 78%; mp: 157–159 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.05 (d, 2H, *J*=6.8 Hz, ArH), 7.95 (d, 1H, *J*=8.8 Hz, ArH), 7.83 (d, 2H, *J*=8.0 Hz, ArH), 7.74 (d, 1H, *J*=7.2 Hz, ArH), 7.64 (t, 1H, *J*=7.2 Hz, ArH), 7.45 (t, 1H, *J*=7.6 Hz, ArH), 7.11 (d, 1H, *J*=6.8 Hz, ArH), 5.93 (s, 1H, CH), 2.71 (d, 1H, *J*=16.0 Hz, CH), 2.43 (d, 1H, *J*=16.0 Hz, CH), 2.28–2.04 (m, 2H, CH), 1.13 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.93 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.9, 173.1, 142.7, 140.7, 136.6, 133.0, 132.9, 132.4, 131.7, 131.4, 129.6, 129.3, 128.7, 128.0, 127.9, 127.6, 127.5, 127.1, 124.6, 123.8, 120.3, 117.7, 69.4, 48.7, 26.9, 26.3, 24.7, 9.3; IR (KBr, ν, cm^{-1}): 3065, 1746, 1666, 1611, 1593, 1558, 1518, 1481, 1458, 1434, 1390, 1370; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{23}Cl_2NNaO_3$, 526.0953 $[M+Na]^+$; found: 526.0942.

*4.2.6. 7-(3,5-Dichlorophenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4f**).* A yellow solid: 0.357 g, yield 71%; mp: 197–199 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.05 (d, 1H, *J*=6.8 Hz, ArH), 7.96–7.83 (m, 5H, ArH), 7.64 (t, 1H, *J*=7.2 Hz, ArH), 7.48 (t, 1H, *J*=7.6 Hz, ArH), 7.09 (d, 1H, *J*=6.8 Hz, ArH), 5.92 (s, 1H, CH), 2.71 (d, 1H, *J*=16.4 Hz, CH), 2.42 (d, 1H, *J*=16.0 Hz, CH), 2.35–2.25 (m, 1H, CH), 2.19–2.09 (m, 1H, CH), 1.13 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.96 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.9, 173.1, 142.7, 140.7, 138.9, 135.7, 131.7, 131.3, 130.0, 129.6, 128.7, 128.0, 127.9, 127.6, 127.1, 126.4, 124.6, 123.8, 120.1, 117.7, 69.3, 48.7, 27.0, 26.3, 24.6, 9.3; IR (KBr, ν, cm^{-1}): 3045, 1741, 1666, 1585, 1571, 1558, 1524, 1507, 1457, 1472, 1417, 1385; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{23}Cl_2NNaO_3$, 526.0953 $[M+Na]^+$; found: 526.0940.

*4.2.7. 7-(4-Bromophenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4g**).* A yellow solid: 0.380 g, yield 74%; mp: 155–157 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, *J*=6.8 Hz, ArH), 7.88–7.82 (m, 4H, ArH), 7.63 (d, 3H, *J*=7.2 Hz, ArH), 7.45 (t, 1H, *J*=7.2 Hz, ArH), 7.05 (d, 1H, *J*=6.8 Hz, ArH), 5.94 (s, 1H, CH), 2.71 (d, 1H, *J*=16.4 Hz, CH), 2.43 (d, 1H, *J*=16.4 Hz, CH), 2.30–2.22 (m, 1H, CH), 2.11–2.01 (m, 1H, CH), 1.13 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.92 (t, 3H, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 173.1, 142.6, 140.7, 136.1, 133.5, 131.7, 131.4, 129.6, 129.0, 128.7, 128.0, 127.9, 127.6, 127.0, 124.5, 123.7, 123.1, 120.1, 117.6, 69.5, 48.7, 26.9, 26.3, 24.7, 9.4; IR (KBr, ν, cm^{-1}): 2965, 1740, 1715, 1667, 1647, 1540, 1519, 1490, 1459, 1382; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{24}BrNNaO_3$, 536.0837 $[M+Na]^+$; found: 536.0851.

*4.2.8. 9,9-Dimethyl-7-(4-nitrophenyl)-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4h**).* A yellow solid: 0.331 g, yield 69%; mp: 247–249 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.51 (d, 2H, *J*=8.8 Hz, ArH), 8.07 (d, 1H, *J*=6.4 Hz, ArH), 8.00 (d, 2H, *J*=8.8 Hz, ArH), 7.85 (d, 2H, *J*=8.0 Hz, ArH), 7.67–7.63 (m, 1H, ArH), 7.47–7.43 (m, 1H, ArH), 7.14 (d, 1H, *J*=6.8 Hz, ArH), 5.99 (s, 1H, CH), 2.73 (d, 1H, *J*=16.8 Hz, CH), 2.45 (d, 1H, *J*=16.4 Hz, CH), 2.24–2.20 (m, 1H, CH), 2.10–2.02 (m, 1H, CH), 1.16 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 0.87 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.9, 173.1, 148.1, 142.6, 142.3, 140.5, 131.7, 131.2, 129.6, 128.7, 128.4, 127.9, 127.8(0), 127.7(7), 127.2, 125.9, 125.1, 124.0, 120.5, 118.1, 69.5, 48.6, 26.9, 26.2, 24.8, 9.4; IR (KBr, ν, cm^{-1}): 2978, 1740, 1666, 1609, 1594, 1522, 1497, 1457, 1385, 1342; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{24}N_2NaO_5$, 503.1583 $[M+Na]^+$; found: 503.1597.

*4.2.9. 9,9-Dimethyl-11-oxo-7-phenyl-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4i**).* A yellow solid: 0.313 g, yield 72%; mp: 182–184 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, *J*=6.4 Hz, ArH), 7.81 (d, 2H, *J*=5.6 Hz, ArH), 7.65 (s, 6H, ArH), 7.43 (t, 1H, *J*=7.2 Hz, ArH), 6.97 (d, 1H, *J*=6.8 Hz, ArH), 5.95 (s, 1H, CH), 2.71 (d, 1H, *J*=16.8 Hz, CH), 2.43 (d, 1H, *J*=16.8 Hz, CH), 2.24–2.18 (m, 1H, CH), 2.08–2.00 (m, 1H, CH), 1.14 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.89 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 172.9, 142.5, 140.8, 136.8, 131.8, 131.5, 130.5, 130.0, 129.6, 128.7, 128.2, 127.8, 127.4, 126.9, 126.8, 124.4, 123.6, 119.9, 117.4, 69.5, 48.7, 26.9, 26.3, 24.8, 9.4; IR (KBr, ν, cm^{-1}): 3067, 1738, 1661, 1611, 1596, 1518, 1457, 1411, 1392, 1350; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{25}NNaO_3$, 458.1732 $[M+Na]^+$; found: 458.1749.

*4.2.10. 9,9-Dimethyl-11-oxo-7-(m-tolyl)-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4j**).* A yellow solid: 0.314 g, yield 70%; mp: 156–158 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.04 (d, 1H, *J*=6.4 Hz, ArH), 7.83–7.80 (m, 2H, ArH), 7.63 (t, 1H, *J*=7.2 Hz, ArH), 7.55 (t, 1H, *J*=8.0 Hz, ArH), 7.46–7.39 (m, 4H, ArH), 7.01 (d, 1H, *J*=7.2 Hz, ArH), 5.93 (s, 1H, CH), 2.71 (d, 1H, *J*=16.0 Hz, CH), 2.47 (d, 1H, *J*=12.4 Hz, CH), 2.42 (s, 3H, CH_3), 2.26–2.12 (m, 2H, CH), 1.11 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.92 (t, 3H, *J*=6.0 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 193.7, 175.6, 147.9, 140.1, 139.4, 137.1, 131.9, 131.8, 130.2, 130.1, 129.5, 128.8, 128.6, 127.8, 127.1, 126.7, 126.6, 124.8, 123.4, 123.3, 119.8, 115.9, 68.3, 47.3, 27.3, 26.3, 25.9, 21.4, 9.5; IR (KBr, ν, cm^{-1}): 3059, 1742, 1666, 1647, 1610, 1568, 1540, 1521, 1489, 1471, 1385; HRMS (ESI): *m*/*z* calcd for: $C_{30}H_{27}NNaO_3$, 472.1889 $[M+Na]^+$; found: 472.1898.

*4.2.11. 9,9-Dimethyl-11-oxo-7-(o-tolyl)-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4k**).* A yellow solid: 0.287 g, yield 64%; mp: 190–192 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.03 (d, 1H, *J*=6.8 Hz, ArH), 7.83–7.79 (m, 2H, ArH), 7.66–7.62 (m, 1H, ArH), 7.58–7.55 (m, 2H, ArH), 7.49–7.48 (m, 1H, ArH), 7.44–7.38 (m, 2H, ArH), 6.69 (d, 1H, *J*=7.2 Hz, ArH), 5.92+5.60 (s, 1H, CH), 2.78–2.66 (m, 1H, CH), 2.46–2.32 (m, 1H, CH), 2.30–2.20 (m, 1H, CH), 2.16–2.12+1.94–1.88 (m, 1H, CH), 1.13 (d, 3H, *J*=4.4 Hz, CH_3), 1.00 (d, 3H, *J*=8.0 Hz, CH_3), 0.95+0.85 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.7(3), 192.6(6), 172.9, 172.6, 142.6, 142.5, 140.8, 140.7, 135.9, 135.5, 135.4, 135.2, 131.9, 131.7(63), 131.7(57), 131.7(3), 131.7(0), 131.6(4), 130.5(9), 130.4, 129.6, 129.5, 128.7, 128.3, 128.2, 128.0(0), 127.9(8), 127.9(5), 127.9(3), 127.8, 127.4(3), 127.4(1), 126.8(4), 126.8(2), 124.1(1), 124.0(6), 123.6, 119.3, 119.1, 117.1, 117.0, 69.5, 69.3, 49.0, 48.4, 27.0, 26.6, 26.3, 26.0, 24.9, 24.3, 17.2, 9.4, 9.3; IR (KBr, ν, cm^{-1}): 3070, 1755, 1693, 1604, 1581, 1553, 1476, 1386, 1357, 1258; HRMS (ESI): *m*/*z* calcd for: $C_{30}H_{27}NNaO_3$, 472.1889 $[M+Na]^+$; found: 472.1903.

*4.2.12. 7-(4-Methoxyphenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4l**).* A yellow solid: 0.358 g, yield 77%; mp: 194–196 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.02 (d, 1H, *J*=6.4 Hz, ArH), 7.81 (d, 2H, *J*=7.6 Hz, ArH), 7.63 (t, 1H, *J*=7.2 Hz, ArH), 7.53 (s, 2H, ArH), 7.43 (t, 1H, *J*=7.2 Hz, ArH), 7.18 (d, 2H, *J*=7.6 Hz, ArH), 6.98 (d, 1H, *J*=6.8 Hz, ArH), 5.88 (s, 1H, CH), 3.89 (s, 3H, OCH_3), 2.72 (d, 1H, *J*=16.4 Hz, CH), 2.39 (d, 1H, *J*=16.4 Hz, CH), 2.31–2.21 (m, 1H, CH), 2.16–2.06 (m, 1H, CH), 1.13 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.93 (t, 3H, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 173.0, 160.2, 142.8, 141.1, 131.8, 131.6, 129.6, 129.3, 128.7, 128.3, 128.1, 127.9, 127.4, 126.8, 124.1, 123.5, 119.9, 117.2, 115.5, 69.4, 56.1, 48.6, 27.0, 26.2, 24.9, 9.4;

IR (KBr, ν, cm^{-1}): 3063, 1741, 1660, 1609, 1515, 1462, 1410, 1297, 1252, 1171; HRMS (ESI): *m/z* calcd for: $C_{30}H_{27}NNaO_4$, 488.1838 $[M+Na]^+$; found: 488.1849.

*4.2.13. 7-(4-Bromobenzyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl propionate (**4m**).* A yellow solid: 0.374 g, yield 71%; mp: 150–152 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.02 (d, 1H, *J*=6.8 Hz, ArH), 7.80 (d, 2H, *J*=8.4 Hz, ArH), 7.64–7.58 (m, 2H, ArH), 7.53 (d, 2H, *J*=8.0 Hz, ArH), 7.48 (t, 1H, *J*=7.6 Hz, ArH), 7.02 (d, 2H, *J*=8.0 Hz, ArH), 6.04 (s, 1H, CH), 5.62 (s, 2H, CH_2), 2.80 (d, 1H, *J*=16.8 Hz, CH), 2.27 (d, 1H, *J*=16.4 Hz, CH), 2.23–2.17 (m, 1H, CH), 2.01–1.91 (m, 1H, CH), 1.08 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 0.85 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.7, 173.6, 142.5, 140.3, 136.4, 132.1, 131.8(3), 131.7(5), 129.5, 128.6, 128.4, 128.2, 127.9, 127.3, 126.8, 124.8, 123.4, 121.0, 120.7, 116.9, 68.7, 48.9, 47.6, 26.9, 25.9, 25.7, 9.1; IR (KBr, ν, cm^{-1}): 3065, 1728, 1681, 1646, 1532, 1498, 1456, 1437, 1388, 1352; HRMS (ESI): *m/z* calcd for: $C_{30}H_{26}BrNNaO_3$, 550.0994 $[M+Na]^+$; found: 550.0978.

*4.2.14. 9,9-Dimethyl-11-oxo-7-phenyl-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl butyrate (**4n**).* A yellow solid: 0.323 g, yield 72%; mp: 196–198 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.05 (d, 1H, *J*=5.6 Hz, ArH), 7.80 (s, 2H, ArH), 7.65 (s, 6H, ArH), 7.41 (t, 1H, *J*=6.8 Hz, ArH), 6.96 (d, 1H, *J*=6.4 Hz, ArH), 5.95 (s, 1H, CH), 2.72 (d, 1H, *J*=16.4 Hz, CH), 2.41 (d, 1H, *J*=16.4 Hz, CH), 2.18–2.14 (m, 1H, CH), 2.02–1.98 (m, 1H, CH), 1.40–1.39 (m, 2H, CH_2), 1.14 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.79 (t, 3H, *J*=6.4 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 172.0, 142.5, 140.8, 136.7, 131.8, 131.5, 130.6, 130.0, 129.6, 128.7, 128.2, 127.8, 127.4, 126.9, 126.7, 124.4, 123.7, 119.9, 117.4, 69.4, 48.6, 35.3, 26.2, 24.9, 18.2, 13.9; IR (KBr, ν, cm^{-1}): 3056, 1755, 1693, 1615, 1523, 1488, 1473, 1465, 1385, 1301; HRMS (ESI): *m/z* calcd for: $C_{30}H_{27}NNaO_3$, 472.1889 $[M+Na]^+$; found: 472.1898.

*4.2.15. 7-(4-Methoxyphenyl)-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydro-7H-acenaphtho[1,2-b]indol-8-yl isobutyrate (**4o**).* A yellow solid: 0.326 g, yield 68%; mp: 140–142 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.03 (d, 1H, *J*=6.8 Hz, ArH), 7.83–7.80 (m, 2H, ArH), 7.63 (t, 1H, *J*=7.2 Hz, ArH), 7.54 (s, 2H, ArH), 7.44 (t, 1H, *J*=7.2 Hz, ArH), 7.18 (d, 2H, *J*=8.4 Hz, ArH), 6.99 (d, 1H, *J*=6.8 Hz, ArH), 5.90 (s, 1H, CH), 3.89 (s, 3H, OCH_3), 2.74 (d, 1H, *J*=16.4 Hz, CH), 2.41–2.40 (m, 1H, CH), 2.38 (d, 1H, *J*=6.0 Hz, CH), 1.14 (s, 3H, CH_3), 1.04 (d, 3H, *J*=7.2 Hz, CH_3), 1.00 (s, 3H, CH_3), 0.94 (d, 3H, *J*=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.8, 175.3, 160.2, 142.7, 141.1, 131.8, 131.6, 129.6, 129.3, 128.7, 128.3, 128.1, 127.9, 127.4, 126.9, 124.1, 123.6, 119.9, 117.2, 115.6, 69.2, 56.1, 48.5, 33.7, 26.2, 24.9, 19.5, 18.9; IR (KBr, ν, cm^{-1}): 3056, 1762, 1664, 1658, 1568, 1489, 1473, 1465, 1386, 1355; HRMS (ESI): *m/z* calcd for: $C_{31}H_{29}NNaO_4$, 502.1994 $[M+Na]^+$; found: 502.2008.

4.3. General procedure for the synthesis of 6a–6f

*4.3.1. 7-(4-Chlorophenyl)-10,10-dimethyl-7H-acenaphtho[1,2-b]indol-11(10H)-one (**6a**).* In a typical experiment procedure, 3-((4-chlorophenyl)amino)-6,6-dimethylcyclohex-2-enone **5a** (1.0 mmol, 0.249 g, 1.0 equiv) and acenaphthylene-1,2-dione **2** (1.0 mmol, 0.182 g, 1.0 equiv) were introduced in a 10-mL Initiator™ reaction vial, acetic anhydride (1.5 mL) was then successively added. Subsequently, the reaction vial was capped and then pre-stirring for 20 s. The mixture was irradiated (Time: 23 min, Temperature: 120 °C; Absorption Level: High; Fixed Hold Time) until TLC revealed that conversion of the starting materials were completed. The reaction mixture was then cooled to room temperature and then diluted with cold water (25 mL). The solid product was collected by Büchner filtration to give pure aromatized indoles **6a**, which was further purified by washing from 95% ethanol.

An orange solid: 0.304 g, yield 77%; mp: 266–268 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.10 (d, 1H, *J*=6.0 Hz, ArH), 7.82–7.81 (m, 6H, ArH), 7.64 (t, 1H, *J*=6.8 Hz, ArH), 7.47 (t, 1H, *J*=6.0 Hz, ArH), 7.22 (d, 1H, *J*=6.0 Hz, ArH), 6.51 (d, 1H, *J*=9.6 Hz, CH), 6.28 (d, 1H, *J*=9.6 Hz, CH), 1.28 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 198.2, 144.7, 144.3, 139.9, 135.3, 134.2, 132.0, 131.4, 130.7, 129.5, 128.6, 128.4, 128.2, 128.0, 127.3, 127.2, 126.0, 123.9, 120.1, 114.2, 112.3, 47.0, 25.7; IR (KBr, ν, cm^{-1}): 3059, 1645, 1609, 1591, 1518, 1492, 1476, 1454, 1433, 1417, 1385, 1374; HRMS (ESI): *m/z* calcd for: $C_{26}H_{19}ClNO$, 396.1155 $[M+H]^+$; found: 396.1167.

*4.3.2. 7-(3,4-Dichlorophenyl)-10,10-dimethyl-7H-acenaphtho[1,2-b]indol-11(10H)-one (**6b**).* An orange solid: 0.292 g, yield 68%; mp: 205–207 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.20 (d, 1H, *J*=2.4 Hz, ArH), 8.10 (d, 1H, *J*=6.8 Hz, ArH), 8.00 (d, 1H, *J*=8.8 Hz, ArH), 7.86–7.82 (m, 3H, ArH), 7.64 (t, 1H, *J*=7.2 Hz, ArH), 7.49 (t, 1H, *J*=7.2 Hz, ArH), 7.25 (d, 1H, *J*=7.2 Hz, ArH), 6.56 (d, 1H, *J*=10.0 Hz, CH), 6.30 (d, 1H, *J*=9.6 Hz, CH), 1.28 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 198.2, 144.8, 144.5, 139.9, 136.3, 133.0, 132.6, 132.5, 132.0, 131.3, 129.5, 128.8, 128.6, 128.1, 128.0, 127.4, 127.3, 127.1, 126.1, 124.0, 120.1, 114.3, 112.3, 47.1, 25.7; IR (KBr, ν, cm^{-1}): 3061, 1738, 1669, 1611, 1519, 1481, 1460, 1434, 1411, 1390, 1349; HRMS (ESI): *m/z* calcd for: $C_{26}H_{18}Cl_2NO$, 430.0765 $[M+H]^+$; found: 430.0749.

*4.3.3. 7-(4-Bromophenyl)-10,10-dimethyl-7H-acenaphtho[1,2-b]indol-11(10H)-one (**6c**).* An orange solid: 0.329 g, yield 75%; mp: 267–269 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.10 (d, 1H, *J*=6.8 Hz, ArH), 7.93 (d, 2H, *J*=8.0 Hz, ArH), 7.82 (t, 2H, *J*=7.2 Hz, ArH), 7.76 (d, 2H, *J*=8.0 Hz, ArH), 7.64 (d, 1H, *J*=7.2 Hz, ArH), 7.47 (d, 1H, *J*=7.2 Hz, ArH), 7.23 (d, 1H, *J*=7.2 Hz, ArH), 6.52 (d, 1H, *J*=10.0 Hz, CH), 6.28 (d, 1H, *J*=10.0 Hz, CH), 1.28 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 198.2, 144.7, 144.2, 139.8, 135.7, 133.7, 132.0, 131.3, 129.5, 128.6(5), 128.6(0), 128.2, 128.0, 127.3, 127.2, 126.1, 123.9, 122.6, 120.1, 114.2, 112.3, 47.0, 25.7; IR (KBr, ν, cm^{-1}): 3055, 1646, 1609, 1584, 1517, 1490, 1454, 1433, 1417, 1385, 1349; HRMS (ESI): *m/z* calcd for: $C_{26}H_{19}BrNO$, 440.0650 $[M+H]^+$; found: 440.0639.

*4.3.4. 10,10-Dimethyl-7-phenyl-7H-acenaphtho[1,2-b]indol-11(10H)-one (**6d**).* An orange solid: 0.267 g, yield 74%; mp: 176–178 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.10 (d, 1H, *J*=6.8 Hz, ArH), 7.84–7.73 (m, 6H, ArH), 7.69–7.62 (m, 2H, ArH), 7.47 (t, 1H, *J*=7.2 Hz, ArH), 7.18 (d, 1H, *J*=6.8 Hz, ArH), 6.51 (d, 1H, *J*=10.0 Hz, CH), 6.28 (d, 1H, *J*=9.6 Hz, CH), 1.28 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 198.2, 144.6, 144.2, 140.0, 136.4, 132.1, 131.5, 130.7, 129.7, 129.5, 128.6, 128.4, 127.9, 127.3, 127.1, 126.5, 125.9, 123.8, 119.9, 114.1, 112.4, 47.0, 25.7; IR (KBr, ν, cm^{-1}): 3043, 1654, 1639, 1580, 1523, 1467, 1429, 1417, 1387, 1366; HRMS (ESI): *m/z* calcd for: $C_{26}H_{20}NO$, 362.1545 $[M+H]^+$; found: 362.1561.

*4.3.5. 10,10-Dimethyl-7-(p-tolyl)-7H-acenaphtho[1,2-b]indol-11(10H)-one (**6e**).* An orange solid: 0.319 g, yield 85%; mp: 238–240 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.08 (d, 1H, *J*=6.0 Hz, ArH), 7.81 (t, 2H, *J*=7.2 Hz, ArH), 7.63 (d, 3H, *J*=7.2 Hz, ArH), 7.52 (d, 2H, *J*=6.4 Hz, ArH), 7.45 (t, 1H, *J*=6.8 Hz, ArH), 7.17 (d, 1H, *J*=6.4 Hz, ArH), 6.48 (d, 1H, *J*=9.6 Hz, CH), 6.25 (d, 1H, *J*=9.2 Hz, CH), 2.48 (s, 3H, CH_3), 1.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 198.1, 144.4, 144.2, 140.1, 139.3, 133.8, 132.1, 131.5, 131.1, 129.5, 128.6, 128.4, 127.9, 127.2, 127.0, 126.2, 125.8, 123.8, 119.9,

114.0, 112.4, 47.0, 25.7, 21.3; IR (KBr, ν, cm^{-1}): 3063, 1736, 1654, 1639, 1568, 1543, 1485, 1476, 1415, 1386; HRMS (ESI): *m/z* calcd for: $C_{27}H_{22}NO$, 376.1701 $[M+H]^+$; found: 376.1718.

*4.3.6. 7-(4-Methoxyphenyl)-10,10-dimethyl-7H-acenaphtho[1,2-b]indol-11(10H)-one (**6f**).* An orange solid: 0.313 g, yield 80%; mp: 240–242 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.08 (d, 1H, *J*=6.8 Hz, ArH), 7.80 (t, 2H, *J*=8.0 Hz, ArH), 7.68 (d, 2H, *J*=8.8 Hz, ArH), 7.65–7.61 (m, 1H, ArH), 7.45 (t, 1H, *J*=7.2 Hz, ArH), 7.25 (d, 2H, *J*=8.8 Hz, ArH), 7.16 (d, 1H, *J*=6.8 Hz, ArH), 6.46 (d, 1H, *J*=10.0 Hz, CH), 6.25 (d, 1H, *J*=9.6 Hz, CH), 3.91 (s, 3H, OCH_3), 1.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 198.1, 160.0, 144.4, 144.3, 140.4, 132.1, 131.6, 129.5, 129.0, 128.6, 128.4, 127.9, 127.8, 127.2, 127.0, 125.6, 123.7, 119.9, 115.7, 113.9, 112.4, 56.1, 46.9, 25.7; IR (KBr, ν, cm^{-1}): 3004, 1644, 1610, 1511, 1477, 1456, 1415, 1385, 1301, 1254; HRMS (ESI): *m/z* calcd for: $C_{27}H_{22}NO_2$, 392.1651 $[M+H]^+$; found: 392.1641.

4.4. General procedure for the synthesis of 8a–8s

*4.4.1. 7-Phenyl-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8a**).* In a typical experiment procedure, 3-(phenylamino)cyclohex-2-enone **7a** (1.0 mmol, 0.187 g, 1.0 equiv) and acenaphthylene-1,2-dione **2** (1.0 mmol, 0.182 g, 1.0 equiv) were introduced in a 10-mL Initiator™ reaction vial, acetic anhydride (1.5 mL) was then successively added. Subsequently, the reaction vial was capped and then pre-stirring for 20 s. The mixture was irradiated (Time: 20 min, Temperature: 120 °C; Absorption Level: High; Fixed Hold Time) until TLC revealed that conversion of the starting materials were completed. The reaction mixture was then cooled to room temperature and then diluted with cold water (25 mL). The solid product was collected by Büchner filtration to give pure esterification indoles **8a**.

An orange solid: 0.274 g, yield 73%; mp: 197–199 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.89 (d, 1H, *J*=8.0 Hz, ArH), 7.84 (d, 2H, *J*=7.6 Hz, ArH), 7.79 (d, 1H, *J*=3.2 Hz, ArH), 7.77–7.75 (m, 2H, ArH), 7.74 (d, 1H, *J*=3.6 Hz, ArH), 7.65 (t, 2H, *J*=8.0 Hz, ArH), 7.52 (t, 1H, *J*=7.2 Hz, ArH), 7.38 (d, 1H, *J*=6.8 Hz, ArH), 7.29 (d, 1H, *J*=8.4 Hz, ArH), 7.22 (t, 1H, *J*=8.0 Hz, ArH), 7.07 (d, 1H, *J*=7.6 Hz, ArH), 2.63 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.8, 144.4, 143.6, 143.4, 137.4, 132.4, 132.2, 130.8, 129.6, 129.0, 128.6, 128.3, 128.0, 126.3, 125.8, 123.3, 121.6, 121.5, 118.2, 117.3, 115.1, 109.6, 22.0; IR (KBr, ν, cm^{-1}): 3045, 1763, 1743, 1638, 1609, 1596, 1568, 1501, 1450, 1369, 1339; HRMS (ESI): *m/z* calcd for: $C_{26}H_{17}NNaO_2$, 398.1157 $[M+Na]^+$; found: 398.1166.

*4.4.2. 7-(4-Chlorophenyl)-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8b**).* An orange solid: 0.311 g, yield 76%; mp: 183–185 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.91–7.89 (m, 2H, ArH), 7.88 (s, 1H, ArH), 7.82 (s, 1H, ArH), 7.80 (s, 1H, ArH), 7.78 (s, 1H, ArH), 7.74 (d, 1H, *J*=6.8 Hz, ArH), 7.65 (t, 1H, *J*=7.2 Hz, ArH), 7.54 (t, 1H, *J*=7.2 Hz, ArH), 7.43 (d, 1H, *J*=7.2 Hz, ArH), 7.31 (d, 1H, *J*=8.0 Hz, ArH), 7.24 (t, 1H, *J*=7.6 Hz, ArH), 7.08 (d, 1H, *J*=7.6 Hz, ArH), 2.63 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.8, 144.2, 143.5, 143.4, 136.3, 133.3, 132.3, 132.1, 130.8, 129.5, 129.0, 128.7, 128.2, 128.1(2), 128.0(6), 125.9, 123.5, 121.8, 121.6, 118.5, 117.3, 115.3, 109.6, 22.0; IR (KBr, ν, cm^{-1}): 3055, 1760, 1654, 1613, 1522, 1498, 1479, 1392, 1356, 1329; HRMS (ESI): *m/z* calcd for: $C_{26}H_{16}ClNNaO_2$, 432.0767 $[M+Na]^+$; found: 432.0754.

*4.4.3. 7-(4-Chlorophenyl)-9-methyl-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8c**).* An orange solid: 0.326 g, yield 77%; mp: 177–179 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.89–7.85 (m, 3H, ArH), 7.82–7.81 (m, 1H, ArH), 7.80–7.79 (m, 1H, ArH), 7.77 (d, 1H, *J*=8.4 Hz, ArH), 7.70 (d, 1H, *J*=6.4 Hz, ArH), 7.65–7.61 (m, 1H, ArH), 7.52 (t, 1H, *J*=6.8 Hz, ArH), 7.38 (d, 1H, *J*=6.8 Hz, ArH), 7.12 (s, 1H, ArH), 6.92 (s, 1H, ArH), 2.61 (s, 3H, CH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.8, 143.7, 143.1, 136.4, 133.5, 133.2, 132.3, 131.9, 130.8, 129.5, 129.0, 128.4, 128.3, 128.2, 128.0, 125.8, 121.5(3), 121.5(0), 118.5, 116.7, 115.3, 109.4, 21.9, 21.7; IR (KBr, ν, cm^{-1}): 3059, 1764, 1629, 1609, 1581, 1496, 1439, 1417, 1366, 1346, 1335; HRMS (ESI): *m/z* calcd for: $C_{27}H_{18}ClNNaO_2$, 446.0924 $[M+Na]^+$; found: 446.0937.

*4.4.4. 7-(4-Methoxyphenyl)-9-methyl-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8d**).* An orange solid: 0.310 g, yield 74%; mp: 185–187 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.85 (d, 1H, *J*=8.0 Hz, ArH), 7.75–7.66 (m, 4H, ArH), 7.61 (t, 1H, *J*=8.0 Hz, ArH), 7.49 (t, 1H, *J*=7.2 Hz, ArH), 7.29–7.27 (m, 3H, ArH), 7.02 (s, 1H, ArH), 6.88 (s, 1H, ArH), 3.92 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.8, 159.5, 144.3, 144.2, 143.0, 133.0, 132.6, 132.0, 130.1, 129.5, 129.0, 128.6, 128.3, 128.0, 127.8, 125.5, 121.2, 117.6, 116.3, 115.8, 115.1, 109.4, 100.0, 56.0, 21.9, 21.7; IR (KBr, ν, cm^{-1}): 3057, 1766, 1609, 1569, 1514, 1479, 1443, 1366, 1335, 1301; HRMS (ESI): *m/z* calcd for: $C_{28}H_{21}NNaO_3$, 442.1419 $[M+Na]^+$; found: 442.1402.

*4.4.5. 7-(4-Chlorophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8e**).* An orange solid: 0.388 g, yield 80%; mp: 223–225 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.95–7.89 (m, 3H, ArH), 7.80 (t, 3H, *J*=7.6 Hz, ArH), 7.75 (d, 1H, *J*=6.4 Hz, ArH), 7.70–7.63 (m, 3H, ArH), 7.55–7.41 (m, 6H, ArH), 7.36 (t, 1H, *J*=7.2 Hz, ArH), 2.65 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.9, 144.9, 144.0, 143.7, 140.4, 136.2, 136.1, 133.3, 132.2, 132.1, 130.9, 129.6, 129.4, 129.0, 128.8, 128.3, 128.1, 127.8, 127.3, 126.0, 121.9, 121.7, 118.4, 116.6, 114.5, 107.4, 22.0; IR (KBr, ν, cm^{-1}): 3036, 1647, 1609, 1522, 1489, 1473, 1457, 1402, 1360, 1347, 1328, 1297; HRMS (ESI): *m/z* calcd for: $C_{32}H_{20}ClNNaO_2$, 508.1080 $[M+Na]^+$; found: 508.1093.

*4.4.6. 7-(4-Bromophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8f**).* An orange solid: 0.407 g, yield 77%; mp: 242–244 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.95–7.86 (m, 5H, ArH), 7.79 (d, 1H, *J*=8.0 Hz, ArH), 7.75 (d, 1H, *J*=6.8 Hz, ArH), 7.70–7.64 (m, 3H, ArH), 7.55–7.51 (m, 2H, ArH), 7.48–7.43 (m, 4H, ArH), 7.36 (t, 1H, *J*=7.2 Hz, ArH), 2.65 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.9, 144.8, 143.9, 143.7, 140.4, 136.6, 136.1, 133.8, 132.2, 132.1, 129.6, 129.4, 129.0, 128.8, 128.5, 128.1, 127.8, 127.3, 126.0, 121.9, 121.8, 118.5, 116.6, 114.5, 107.4, 22.0; IR (KBr, ν, cm^{-1}): 3054, 1760, 1609, 1598, 1564, 1496, 1447, 1434, 1398, 1365, 1346, 1298; HRMS (ESI): *m/z* calcd for: $C_{32}H_{20}BrNNaO_2$, 552.0575 $[M+Na]^+$; found: 552.0598.

*4.4.7. 9-Phenyl-7-(p-tolyl)-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8g**).* An orange solid: 0.344 g, yield 74%; mp: 218–220 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.88 (d, 1H, *J*=8.0 Hz, ArH), 7.75 (t, 4H, *J*=9.2 Hz, ArH), 7.65 (t, 3H, *J*=7.6 Hz, ArH), 7.55–7.49 (m, 3H, ArH), 7.47–7.40 (m, 4H, ArH), 7.37–7.33 (m, 2H, ArH), 2.65 (s, 3H, CH_3), 2.49 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.9, 145.2, 144.1, 143.7, 140.5, 138.6, 135.8, 134.7, 132.3, 131.3, 129.6, 129.4, 129.0, 128.6, 128.3, 128.0, 127.7, 127.2, 126.2, 125.8, 121.7, 121.5, 117.9, 116.5, 114.2, 107.5, 22.0, 21.3; IR (KBr, ν, cm^{-1}): 3050, 1762, 1610, 1597, 1565, 1517, 1479, 1448, 1436, 1420, 1364, 1334; HRMS (ESI): *m/z* calcd for: $C_{33}H_{23}NNaO_2$, 488.1626 $[M+Na]^+$; found: 488.1641.

*4.4.8. 7-Benzyl-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl acetate (**8h**).* An orange solid: 0.307 g, yield 66%; mp: 223–225 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.94 (d, 2H, *J*=6.8 Hz, ArH), 7.88 (d, 1H, *J*=8.4 Hz, ArH), 7.76 (t, 3H, *J*=8.0 Hz, ArH), 7.69 (d, 1H, *J*=6.0 Hz, ArH), 7.65–7.56 (m, 2H, ArH), 7.49 (t, 2H, *J*=7.2 Hz, ArH), 7.37–7.30 (m, 6H, ArH), 7.25–7.24 (m, 1H, ArH), 5.96 (s, 2H, CH_2), 2.63 (s, 3H,

CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 169.9, 145.8, 144.3, 143.6, 140.6, 137.9, 135.0, 132.7, 132.3, 129.5, 129.4, 129.3, 129.0, 128.4, 128.1, 128.0, 127.6, 127.2, 127.1, 125.4, 122.2, 121.0, 117.0, 116.2, 113.4, 107.7, 48.6, 22.0; IR (KBr, ν, cm^{-1}): 3030, 1763, 1609, 1564, 1498, 1452, 1436, 1417, 1369, 1355, 1335; HRMS (ESI): *m*/*z* calcd for: $C_{33}H_{23}NNaO_2$, 488.1626 $[M+Na]^+$; found: 488.1611.

*4.4.9. 7-(4-Chlorophenyl)-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8i**).* A red-orange solid: 0.300 g, yield 71%; mp: 155–157 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.91–7.87 (m, 3H, ArH), 7.81–7.77 (m, 3H, ArH), 7.70 (d, 1H, *J*=6.8 Hz, ArH), 7.64 (t, 1H, *J*=7.6 Hz, ArH), 7.53 (t, 1H, *J*=7.2 Hz, ArH), 7.42 (d, 1H, *J*=6.8 Hz, ArH), 7.30 (d, 1H, *J*=8.0 Hz, ArH), 7.23 (t, 1H, *J*=8.0 Hz, ArH), 7.08 (d, 1H, *J*=7.6 Hz, ArH), 3.02–2.97 (m, 2H, CH_2), 1.28 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.2, 144.2, 143.5(3), 143.5(0), 136.3, 133.3, 132.3, 132.1, 130.8, 129.6, 129.0, 128.7, 128.2, 128.1(3), 128.0(6), 125.9, 123.5, 121.8, 121.6, 118.5, 117.3, 115.2, 109.5, 27.9, 9.5; IR (KBr, ν, cm^{-1}): 3053, 1752, 1608, 1595, 1568, 1498, 1450, 1420, 1401, 1339; HRMS (ESI): *m*/*z* calcd for: $C_{27}H_{18}ClNNaO_2$, 446.0924 $[M+Na]^+$; found: 446.0936.

*4.4.10. 7-(4-Bromophenyl)-9-methyl-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8j**).* A red solid: 0.332 g, yield 69%; mp: 195–197 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.93 (d, 2H, *J*=8.4 Hz, ArH), 7.87 (d, 1H, *J*=8.0 Hz, ArH), 7.80–7.75 (m, 3H, ArH), 7.67–7.60 (m, 2H, ArH), 7.51 (t, 1H, *J*=7.2 Hz, ArH), 7.39 (d, 1H, *J*=6.8 Hz, ArH), 7.12 (s, 1H, ArH), 6.92 (s, 1H, ArH), 3.01–2.95 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 1.28 (t, 3H, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.2, 143.6(4), 143.6(0), 143.1, 136.8, 133.7, 133.6, 132.3, 131.9, 129.5, 128.9, 128.5, 128.4, 128.3, 128.0, 125.9, 121.6, 121.5, 118.6, 116.6, 115.3, 109.4, 27.9, 21.7, 9.5; IR (KBr, ν, cm^{-1}): 3034, 1754, 1622, 1608, 1583, 1494, 1467, 1442, 1413, 1396, 1375, 1345; HRMS (ESI): *m*/*z* calcd for: $C_{28}H_{20}BrNNaO_2$, 504.0575 $[M+Na]^+$; found: 504.0589.

*4.4.11. 9-Methyl-7-(p-tolyl)-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8k**).* A red solid: 0.354 g, yield 85%; mp: 140–142 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.84 (d, 1H, *J*=8.0 Hz, ArH), 7.73 (d, 1H, *J*=8.0 Hz, ArH), 7.68–7.59 (m, 4H, ArH), 7.54 (d, 2H, *J*=8.0 Hz, ArH), 7.49 (t, 1H, *J*=7.2 Hz, ArH), 7.32 (d, 1H, *J*=6.8 Hz, ArH), 7.06 (s, 1H, ArH), 6.89 (s, 1H, ArH), 3.00–2.95 (m, 2H, CH_2), 2.49 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 1.28 (t, 3H, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.2, 144.0, 143.9, 143.1, 138.5, 134.9, 133.2, 132.6, 132.0, 131.2, 129.5, 128.9, 128.6, 128.3, 128.0, 126.1, 125.6, 121.3, 121.2, 118.0, 116.3, 115.2, 109.4, 27.9, 21.7, 21.3, 9.5; IR (KBr, ν, cm^{-1}): 3042, 1741, 1660, 1609, 1515, 1462, 1446, 1410, 1391, 1349; HRMS (ESI): *m*/*z* calcd for: $C_{29}H_{23}NNaO_2$, 440.1626 $[M+Na]^+$; found: 440.1612.

*4.4.12. 7-(4-Chlorophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8l**).* A red-orange solid: 0.369 g, yield 74%; mp: 219–221 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.97–7.91 (m, 3H, ArH), 7.83–7.79 (m, 3H, ArH), 7.71–7.64 (m, 4H, ArH), 7.56–7.44 (m, 6H, ArH), 7.38–7.35 (m, 1H, ArH), 3.05–3.02 (m, 2H, CH_2), 1.31 (t, 3H, *J*=6.4 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.3, 144.9, 144.0, 143.8, 140.4, 136.2, 136.1, 133.3, 132.2, 132.1, 130.9, 129.6, 129.4, 129.0, 128.8, 128.3, 128.1, 127.8, 127.3, 126.0, 121.9, 121.7, 118.4, 116.6, 114.5, 107.4, 28.0, 9.5; IR (KBr, ν, cm^{-1}): 3045, 1749, 1608, 1597, 1564, 1501, 1449, 1437, 1418, 1377, 1344; HRMS (ESI): *m*/*z* calcd for: $C_{33}H_{22}ClNNaO_2$, 522.1237 $[M+Na]^+$; found: 522.1249.

*4.4.13. 7-(3,5-Dichlorophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8m**).* A red solid: 0.400 g, yield 75%; mp: 194–196 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.09 (s, 2H, ArH), 7.93–7.91 (m, 2H, ArH), 7.81 (d, 1H, *J*=8.4 Hz, ArH), 7.74–7.64 (m, 4H, ArH), 7.59–7.53 (m, 2H, ArH), 7.49–7.44 (m, 3H, ArH), 7.41–7.35 (m, 2H, ArH), 3.05–3.00 (m, 2H, CH_2), 1.30 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.3, 144.7, 144.0, 143.7, 140.4, 139.6, 136.3, 135.9, 132.1, 132.0, 129.6, 129.4, 129.0, 128.8, 128.2, 128.1, 127.8, 127.4, 126.2, 125.8, 121.9, 121.7, 118.9, 116.6, 114.8, 107.5, 28.0, 9.5; IR (KBr, ν, cm^{-1}): 3045, 1741, 1666, 1610, 1586, 1571, 1523, 1509, 1472, 1458, 1431, 1394, 1368, 1352; HRMS (ESI): *m*/*z* calcd for: $C_{33}H_{21}Cl_2NNaO_2$, 556.0847 $[M+Na]^+$; found: 556.0862.

*4.4.14. 7-(4-Bromophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8n**).* A red-orange solid: 0.380 g, yield 70%; mp: 197–199 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.97–7.89 (m, 5H, ArH), 7.81 (d, 1H, *J*=8.0 Hz, ArH), 7.74–7.64 (m, 4H, ArH), 7.57–7.52 (m, 2H, ArH), 7.49–7.44 (m, 4H, ArH), 7.36 (t, 1H, *J*=6.8 Hz, ArH), 3.05–3.00 (m, 2H, CH_2), 1.31 (t, 3H, *J*=7.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.3, 144.8, 143.9, 143.8, 140.4, 136.6, 136.1, 133.8, 132.2, 132.1, 129.6, 129.4, 129.0, 128.8, 128.6, 128.1(3), 128.0(9), 127.8, 127.3, 126.0, 121.9, 121.8, 121.7, 118.5, 116.6, 114.5, 107.4, 28.0, 9.5; IR (KBr, ν, cm^{-1}): 3045, 1749, 1608, 1597, 1564, 1500, 1449, 1437, 1419, 1399, 1345; HRMS (ESI): *m*/*z* calcd for: $C_{33}H_{22}BrNNaO_2$, 566.0732 $[M+Na]^+$; found: 566.0755.

*4.4.15. 9-Phenyl-7-(p-tolyl)-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8o**).* A red-orange solid: 0.374 g, yield 78%; mp: 167–169 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.89 (d, 1H, *J*=8.0 Hz, ArH), 7.80–7.75 (m, 3H, ArH), 7.71–7.62 (m, 4H, ArH), 7.57–7.50 (m, 3H, ArH), 7.47–7.44 (m, 3H, ArH), 7.40–7.33 (m, 3H, ArH), 3.05–2.99 (m, 2H, CH_2), 2.50 (s, 3H, CH_3), 1.31 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.3, 145.2, 144.1, 143.8, 140.5, 138.7, 135.8, 134.7, 132.3(3), 132.2(9), 131.3, 129.6, 129.4, 129.0, 128.6, 128.3, 128.0, 127.7, 127.2, 126.2, 125.8, 121.7, 121.4, 117.9, 116.5, 114.2, 107.4, 28.0, 21.3, 9.5; IR (KBr, ν, cm^{-1}): 3032, 1750, 1607, 1565, 1517, 1483, 1448, 1436, 1418, 1379, 1340; HRMS (ESI): *m*/*z* calcd for: $C_{34}H_{25}NNaO_2$, 502.1783 $[M+Na]^+$; found: 502.1794.

*4.4.16. 7-Benzyl-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl propionate (**8p**).* A red solid: 0.321 g, yield 67%; mp: 219–221 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.97–7.89 (m, 3H, ArH), 7.78–7.74 (m, 3H, ArH), 7.65–7.58 (m, 3H, ArH), 7.49 (t, 2H, *J*=7.6 Hz, ArH), 7.38–7.26 (m, 6H, ArH), 7.26–7.22 (m, 1H, ArH), 5.98 (s, 2H, CH_2), 3.02–2.97 (m, 2H, CH_2), 1.29 (t, 3H, *J*=7.6 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 173.3, 145.7, 144.3, 143.6, 140.5, 137.9, 135.0, 132.7, 132.2, 129.5, 129.4, 129.2, 128.9, 128.4, 128.1, 128.0, 127.6, 127.2, 127.1, 125.4, 122.2, 120.9, 117.0, 116.1, 113.3, 107.7, 48.6, 27.9, 9.5; IR (KBr, ν, cm^{-1}): 3028, 1759, 1731, 1649, 1609, 1568, 1497, 1477, 1452, 1431, 1418, 1354, 1333; HRMS (ESI): *m*/*z* calcd for: $C_{34}H_{25}NNaO_2$, 502.1783 $[M+Na]^+$; found: 502.1796.

*4.4.17. 7-(4-Chlorophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl butyrate (**8q**).* A red-orange solid: 0.354 g, yield 69%; mp: 176–178 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.93–7.88 (m, 3H, ArH), 7.81–7.79 (m, 3H, ArH), 7.73–7.63 (m, 4H, ArH), 7.51–7.35 (m, 7H, ArH), 2.97 (s, 2H, CH_2), 1.82–1.81 (m, 2H, CH_2), 1.09 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 172.4, 144.8, 143.9, 143.7, 140.4, 136.2, 136.1, 133.3, 132.2, 132.1, 130.9, 129.5, 129.4, 128.9, 128.7, 128.2, 128.1, 128.1, 127.8, 127.3, 126.0, 121.8, 121.7, 118.5, 116.6, 114.5, 107.4, 36.2, 18.4, 14.0; IR (KBr, ν, cm^{-1}): 3055, 1763, 1645, 1619, 1586, 1481, 1470, 1451, 1416, 1358; HRMS (ESI): *m*/*z* calcd for: $C_{34}H_{24}ClNNaO_2$, 536.1393 $[M+Na]^+$; found: 536.1408.

*4.4.18. 7-(4-Bromophenyl)-9-methyl-7H-acenaphtho[1,2-b]indol-11-yl isobutyrate (**8r**).* A red-orange solid: 0.347 g, yield 70%; mp: 159–161 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.93 (d, 2H, *J*=6.8 Hz, ArH), 7.86 (d, 1H, *J*=7.2 Hz, ArH), 7.79–7.74 (m, 3H, ArH),

7.64–7.61 (m, 2H, ArH), 7.50 (s, 1H, ArH), 7.39–7.38 (m, 1H, ArH), 7.12 (s, 1H, ArH), 6.88 (s, 1H, ArH), 3.27–3.24 (m, 1H, CH), 2.41 (s, 3H, CH_3), 1.40 (d, 6H, J=5.2 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 175.9, 143.7, 143.6, 143.3, 136.8, 133.7, 133.6, 132.4, 131.9, 129.5, 128.8, 128.5, 128.3, 128.1, 125.9, 121.6, 121.4, 118.6, 116.4, 115.4, 109.4, 100.0, 34.2, 31.1, 21.7, 19.5; IR (KBr, ν, cm^{-1}): 3036, 1757, 1623, 1607, 1582, 1514, 1482, 1444, 1414, 1345; HRMS (ESI): m/z calcd for: $C_{29}H_{22}BrNNaO_2$, 518.0732 $[M+Na]^+$; found: 518.0756.

*4.4.19. 7-(4-Chlorophenyl)-9-phenyl-7H-acenaphtho[1,2-b]indol-11-yl isobutyrate (**8s**).* A red-orange solid: 0.328 g, yield 64%; mp: 175–177 °C; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.96–7.90 (m, 3H, ArH), 7.80 (t, 3H, J=7.6 Hz, ArH), 7.71–7.64 (m, 4H, ArH), 7.55–7.38 (m, 7H, ArH), 3.31–3.26 (m, 1H, CH), 1.44 (d, 6H, J=6.4 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 175.9, 144.9, 144.0, 143.9, 140.4, 136.2, 136.1, 133.4, 132.2, 132.1, 130.9, 129.6, 129.4, 128.8(4), 128.7(8), 128.3, 128.1(3), 128.0(9), 127.8, 127.4, 126.0, 121.9, 121.6, 118.4, 116.7, 114.3, 107.4, 34.3, 19.5; IR (KBr, ν, cm^{-1}): 3051, 1732, 1678, 1579, 1546, 1503, 1494, 1473, 1389, 1354; HRMS (ESI): m/z calcd for: $C_{34}H_{24}ClNNaO_2$, 536.1393 $[M+Na]^+$; found: 536.1411.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.06.058.

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19. Crystal data for **3j**: $C_{27}H_{23}NO_3$, Mr=409.46, Monoclinic, a=13.7175(14) Å, b=16.5978(16) Å, c=18.6764(18) Å, U=4250.7(7) $Å^3$, T=298(2) K, space group P2(1)/c, Z=8, 7428 reflections measured, 7428 unique (R_{int}=0.0000) which were used in all calculation. The final $wR(F_2)$ was 0.3590 (all data)
20. Crystal data for **4f**: $C_{29}H_{23}Cl_2NO_3$, Mr=504.38, Triclinic, a=10.3883(11) Å, b=10.7901(12) Å, c=13.1361(15) Å, U=1260.8(2) $Å^3$, T=298(2) K, space group P-1, Z=2, 6436 reflections measured, 4370 unique (R_{int}=0.0292) which were used in all calculation. The final $wR(F_2)$ was 0.1150 (all data).
21. Crystal data for **6c**: $C_{26}H_{18}BrNO$, Mr=440.32, Monoclinic, a=9.2942(8) Å, b=11.9911(11) Å, c=17.9266(17) Å, U=1996.0(3) $Å^3$, T=293(2) K, space group P2(1)/c, Z=4, 12878 reflections measured, 3518 unique (R_{int}=0.1012) which were used in all calculation. The final $wR(F_2)$ was 0.1131 (all data).
22. Crystal data for **8e**: $C_{32}H_{20}ClNO_2$, Mr=485.94, Monoclinic, a=12.5369(9) Å, b=25.344(2) Å, c=7.6693(6) Å, U=2334.2(3) $Å^3$, T=298(2) K, space group P2(1)/c, Z=4, 11671 reflections measured, 4093 unique (R_{int}=0.0825) which were used in all calculation. The final $wR(F_2)$ was 0.1252 (all data).