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Photoredox Generated Vinyl Radicals: Synthesis of Bisindoles and *β*-Carbolines

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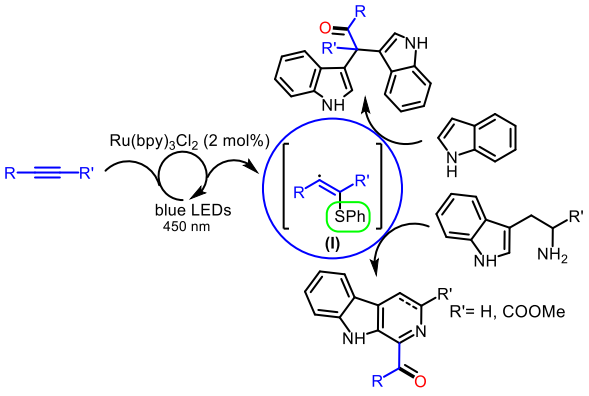


ABSTRACT: A photoredox catalyzed approach enabling use of alkynes as surrogate of 2-oxoaldehydes/1,2-diones is reported. The method overcomes the difficulty associated with application of unsubstituted aliphatic *α*-oxoaldehydes, which has hitherto limited their general use. Indoles, tryptamine and tryptophan methyl ester participated in the reaction to give a variety of *α*-oxo based analogues. Quantum yield investigations support a radical chain mechanism.

INTRODUCTION

Arylglyoxals (AGs) like other α-oxo compounds represent valuable starting materials to access a diverse array of skeletons.[1] Of particular intrigue is the electron-withdrawing characteristic of carbonyl group, which imparts divergent reactive behavior to both aldehyde and ketone functional groups. The reaction around AGs either involve nucleophilic addition,[2] condensation[3] and cross coupling reactions[4] on aldehydic group or both carbonyls encompassing transformations such as Biginelli and Petasis reactions (Figure 1).[5] However, a key inadequacy associated with all the synthetic routes towards AGs include the failure to generate aliphatic products as (i) owing to its unsubstituted α-position it may act either as a nucleophile or electrophile, thereby leading to formation of side products, (ii) the comparable reactivity of two electrophilic centers viz., aldehyde and ketone can result in mixture of regioisomers and (iii) most importantly the synthesis of aliphatic α-oxoaldehyde is very difficult to achieve which limits their use as starting material. In this regard, thiol promoted photoredox reactions,[6] and addition reactions through thiyl radicals are well known on a wide range of unsaturated systems such as alkenes, isonitriles, thiocarbonyls and particularly to alkynes through vinyl radical (**I**) has generated highly regio- and stereoselective products.[7] Unlike alkenes, the vinyl radicals generated from alkynes have capability of undergoing further reactions, however, their application as the surrogate of α-oxoaldehydes/1,2-dicarbonyls has no precedence. As an overarching goal of this work we hoped to demonstrate that photoredox generated vinyl radical (**I**) can provide a complementary approach to aliphatic glyoxals which can give a new dimension to the area of 1,2-dicarbonyls.

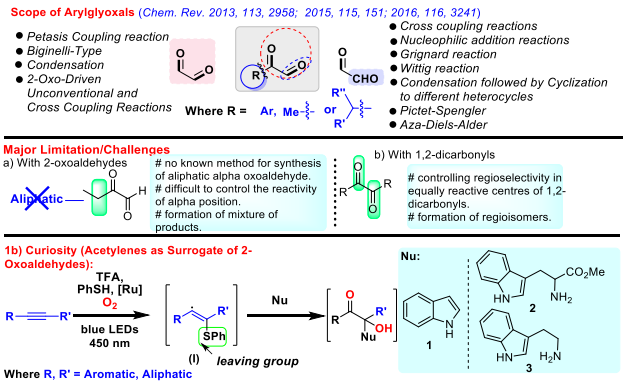


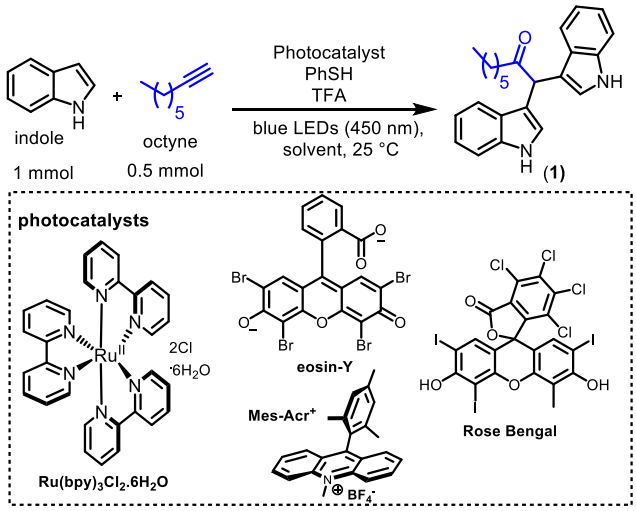
Figure 1. Alkynes as precursors of 2-oxoaldehydes and 1,2-diones.

Thus, in continuation of our interests,[8] we report a solution under which thiol mediated photoredox-catalyzed reaction of alkynes led to synthesis of different valuable *N*-heterocyles. The paramount feature of the present method is its selectivity/general applicability to both aromatic and aliphatic systems. Despite, reports in the bisindolylation reactions around simple arylglyoxals, acetophenones and styrenes (Figure 1),[9] there are no reports on the reaction of indoles that could be highly regioselective and applicable to different 1,2-dicarbonyls. Furthermore, different *β*-carbolines and dihydro-*β*-carbolines could be easily generated by Pictet-Spengler reaction of tryptophan methylester and tryptamine with different alkynes.

RESULTS AND DISCUSSION

Our efforts initiated with the reaction of octyne and indole as model substrates. The reaction was irradiated under blue LEDs in presence of thiophenol (PhSH) and trifluoroacetic acid (TFA) with $Ru(bpy)_3Cl_2.6H_2O$ as photocatalyst using CH_3CN as solvent (Table 1, entry 1). To our delight the reaction led to the formation of bisindole derivative (**1**) in 67% yields (entry 1). The change of solvents to CH_3OH and 1,4 dioxane caused a drop in reaction yields, whereas no product formation was observed in DMSO (Table 1, entries 2-4). The use of mesitylacridinium tetrafluoroborate (Mes-Acr$^+BF_4^-$), eosin-Y, and Rose-Bengal as photocatalyst gave the corresponding product (**1**), in 37, 46 and 15% yields respectively (Table 1, entries 5-7). The presence of thiophenol, TFA, photocatalyst and light was critical as there was either no product formation or in traces in their absence (Table 1, entries 8-11). Notably, the use of TFA in excess of 10 mol% resulted in indole dimer and trimer as side products.[10]

Table 1. Optimization of Reaction Conditions[a]



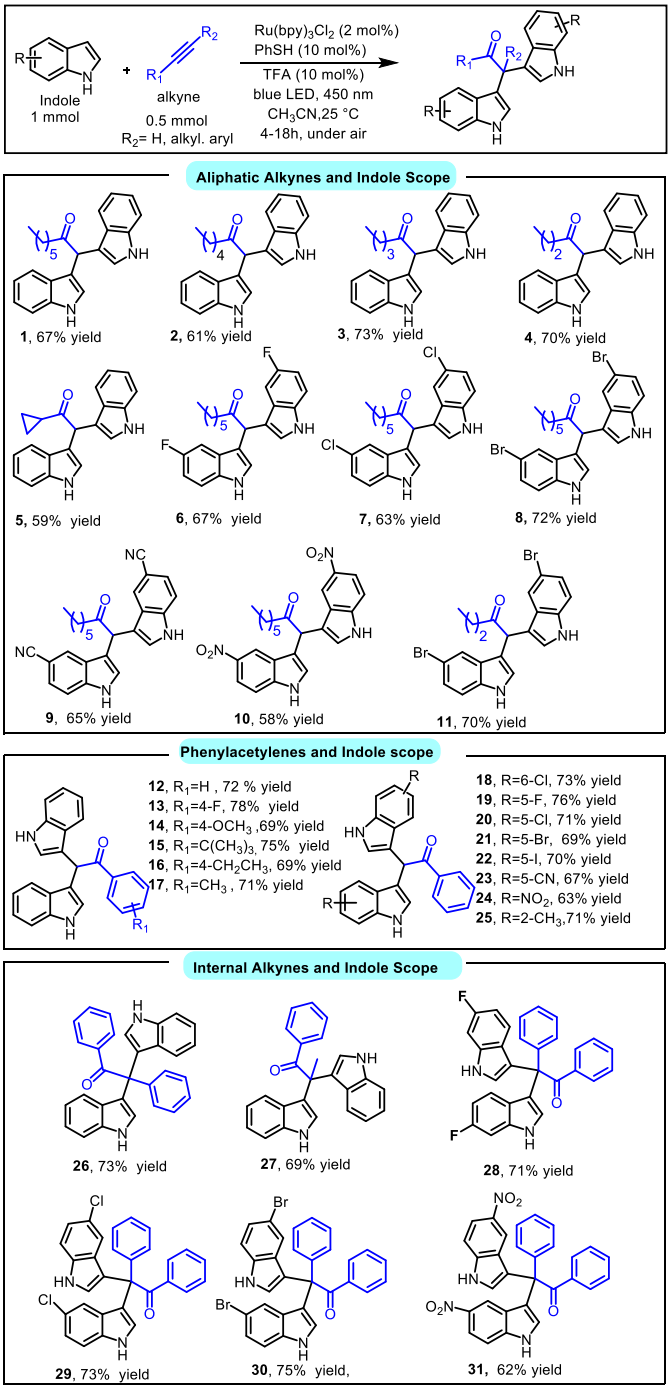
entry	conditions	photocatalyst	solvent	yield (%) *
1	as shown	$Ru(bpy)_3Cl_2$	CH_3CN	67
2	as shown	$Ru(bpy)_3Cl_2$	CH_3OH	25
3	as shown	$Ru(bpy)_3Cl_2$	1,4-dioxane	43
4	as shown	$Ru(bpy)_3Cl_2$	DMSO	ND
5	as shown	Mes-$Acr^+BF_4^-$	CH_3CN	37
6	as shown	eosin-Y	CH_3CN	46
7	as shown	Rose Bengal	CH_3CN	15
8	no thiophenol	$Ru(bpy)_3Cl_2$	CH_3CN	ND
9	no TFA	$Ru(bpy)_3Cl_2$	CH_3CN	10
10	as shown	no photocatlyst	CH_3CN	traces
11	as shown	no light	CH_3CN	traces

[a]Performed with photocatalyst (2 mol%), thiophenol (0.1 mmol), trifluoroacetic acid (TFA, 0.1 mmol); temp: 25 °C; solvent (2ml), under air, time: 18 h.; *Isolated yields.

We next investigated the scope of the reaction with different alkynes and indoles (Scheme 1). The reaction of indole with heptyne, hexyne, pentyne and cyclopropyl acetylene proceeded smoothly to give corresponding derivatives (**2-5**) in 61-73% yields. The 5- F, Cl, Br, CN and NO_2 indole were also found amenable to present reaction protocol producing (**6-10**) in good yields. The reaction of 5-bromoindole with pentyne gave (**11**) in 70% yields. We also studied the reaction viability with different phenylacetylenes and indoles. The reaction of phenylacetylene, 4-F, 4-OMe and 4-alkyl-substituted (*tert*-butyl, ethyl and methyl) phenylacetylene proceeded in a facile manner to produce (**12-17**) in good yields. Also, various indoles such as 6-Cl and 5-F, Cl, Br, I, CN, NO_2 indoles served as suitable substrates with phenylacetylene to give the desired products (**18-24**). The reaction with 2-methylindole also produced (**25**) in 71% yield. We further examined the feasibility of present reaction with internal alkynes. Notably, a

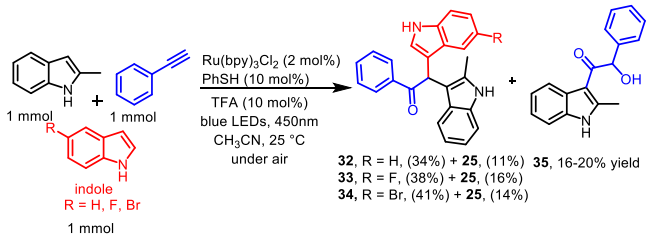
comparable reaction scenario with diketones would probably lead to the formation of regiosisomers with challenge of handling unsusbstituted α- position in aliphatic chains. The diaryl and arylalkyl alkynes viz., diphenylacetylene and 1-phenyl-1-propyne gave corresponding products (**26-27**) in 73 and 69% yields. Furthermore, different indoles viz., 6-F and 5-Cl, Br and 5-NO_2 indoles produced (**28-31**) in 62-75% yield.

Scheme 1. Substrate Scope with Different Alkynes and Indoles



The cross-coupling of two different indoles was also studied (Scheme 2). The reaction of phenylacetylene with 2-methylindole and indole/5-flouro/5-bromo indole led to the formation of asymmetrical products (**32-34**) in 34-41% yields accompanying self coupled product (**25**) and monohydroxy indole product (**35**) as side products. This implies that monohydroxy indole is a possible intermediate in the reaction.

Scheme 2. Cross Coupling of Indoles.



A plausible reaction mechanism is proposed in figure 2. The reaction initiates upon reductive quenching of photoexcited $Ru(bpy)_3^{+2}$ (**36**) by thiophenol which affords the thiyl radical cation (**39**) that subsequently deprotonates to form thiyl radical (**40**).[11] $Ru(bpy)_3^{+2}$ is regenerated by molecular oxygen.[12] The reactive thiyl radical adds to alkyne generating vinyl radical (**41**),[13] which undergo oxygen insertion to give superoxide radical (**42**).[14] The radical **42** can undergo intermolecular cycloaddition with concomitant release of thiyl radical to form intermediate (**43**).[15] The nucleophilic addition of C-3 of indole gives intermediate (**44**), which on subsequent dehydration in presence of TFA generates intermediate (**45**).[16,9b,c,e] The conjugate addition of another molecule of indole followed by deprotonation gives the final product. The incorporation of $^{18}O_2$ in the corresponding product evidenced by LC-MS studies implies that oxygen in the product is sourced from atmospheric oxygen. The Stern−Volmer analysis revealed that the photoluminescence of $Ru(bpy)_3Cl_2$ was quenched by thiophenol in CH_3CN at 25 °C. Furthermore, reaction quantum yields of 23.9 shows that reaction propagates *via* radical chain mechanism. Moreover, complete inhibition of the reaction in presence of radical-quencher TEMPO also indicates its radical nature (see supporting information).

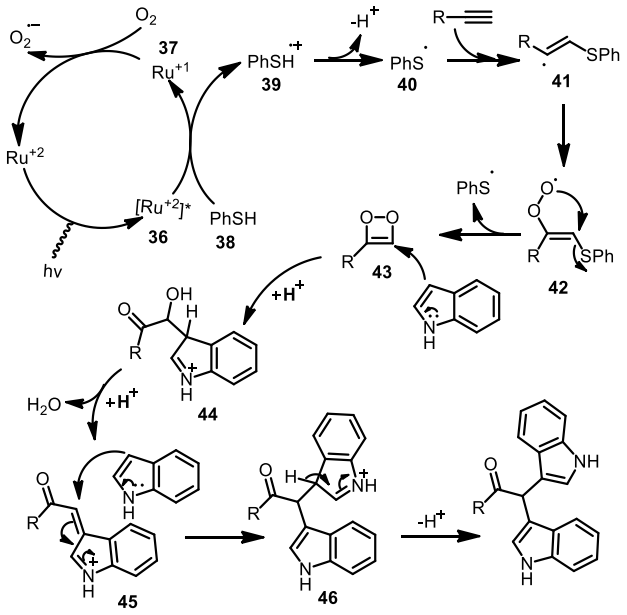
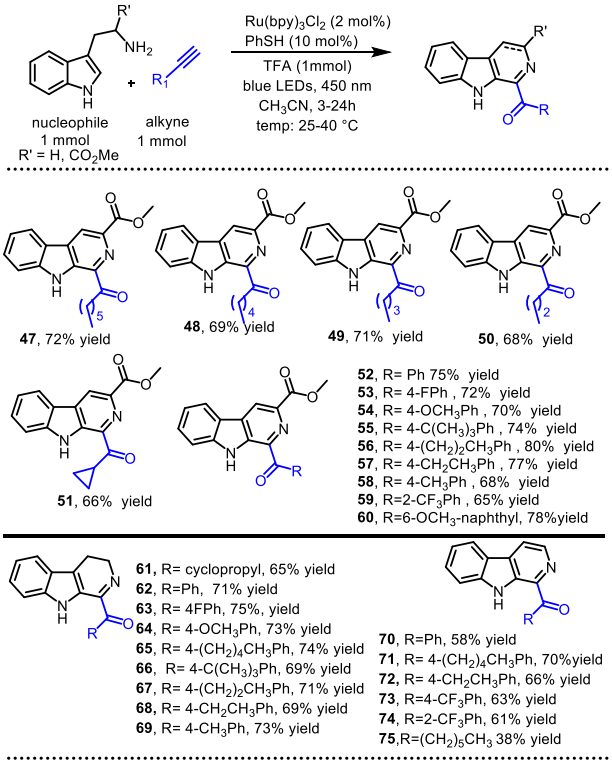


Figure 2. Plausible mechanism

We were further intrigued to explore if this reaction can be expanded to other nucleophiles. In this regard, we chose a related indole substrate, tryptophan methyl ester, which is expected to give *β*-carbolines showcasing C-N bond formation instead of C-C bond. Notably, the synthesis of *β*-carbolines (pyrido[3,4-b]indoles) is one of the most addressed problems in the synthetic organic chemistry, owing to their presence in a large number of natural products and medicinally important molecules.[17] Over the years many approaches have been developed for their synthesis, including reactions such as Bischler-Napieralski,[18] Graebe-Ullmann[19] and Pictet-Spengler reaction.[20] Particularly, Pictet-Spengler reaction of tryptamines has been used to access cores of almost all the monoterpene indole alkaloids.[21] Conspicuously, synthesis of *β*-carbolines with oxo-substitution at C-1, with aliphatic side chain remains hitherto unaddressed. The reaction of tryptophan methyl ester with octyne as expected produced indolocarbazole (**47**) in 72% yields (Scheme 3). Moreover, the reaction with heptyne, hexyne, pentyne as well as cyclopropyl acetylene produced (**48-51**) in 66-71% yields. The reaction was also found agreeable to 4-F, -OMe, 4-alkyl (*tert*-butyl, propyl, ethyl and methyl), and 2-CF_3 as substituent to give (**53-59**) in 65-80% yields. Also, 6-methoxynaphthyl acetylene afforded (**60**) in 78% yields. Remarkably, the reaction of tryptamine with cyclopropyl acetylene instead led to the formation of dihydro-*β*-carboline (**61**) as exclusive product in 65% yield. This observation was significant as previous reports show them as either an

intermediate in low yields or it forms *in situ* which immediately aromatizes.[22] Also, the reaction with 4-F, OMe, pentyl, *tert*-butyl, propyl, ethyl and methyl phenylacetylene proceeded smoothly to generate dihydro-*β*-carbolines (**63-69**) in 69-75% yields. Completely aromatized products with tryptamine (**70-75**) could be easily obtained by increasing the reaction temperature to 40 °C.

Scheme 3. Substrate Scope of Alkynes with Tryptophan methylester and Tryptamine.



CONCLUSION

In conclusion, we have developed a visible light mediated aerobic oxidative conversion of acetylenes to access a wide variety of aliphatic *α*-oxo analogues from indoles, tryptamine and tryptophan methyl ester. The method opens a new window for studying the unexplored reactivity of aliphatic *α*-oxo compounds owing to the reactive nature of *α*-carbon. It would be pertinent to mention that having *α*-CH_2 to carbonyl makes it available for an extensive array of reactions. Furthermore, the reaction is regioselective, easy to set up with broad substrate scope and excellent functional group tolerance. We anticipate that the synthetic utility it offers in terms of overcoming the limitations of AGs will lead to com-

plex heterocycles synthesis and late stage modifications/functionalizations. The further reactivity and applicability of this reaction system is currently under investigation in our laboratory.

EXPERIMENTAL SECTION

General Information. All reactions were conducted in oven-dried glasswares. All reactions were irradiated using blue light-emitting diode (LED) array. ^{1}H and ^{13}C NMR spectra were recorded on FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Mass spectra were obtained by using Q-TOF-LC/MS spectrometer using electron spray ionization.

General experimental procedure: To an oven dried 30 ml glass vial, containing starting compounds indole (2 equiv) /tryptophan methyl ester/ tryptamine (1 equiv) in CH_3CN, was added alkyne (1 equiv), thiophenol (0.1 equiv), trifluoroacetic acid (0.1 equiv for indoles/ 1 equiv for β-carbolines synthesis) and $Ru(bpy)_3Cl_2$ (2 mol%) with continuous stirring under air. The reaction mixture was then irradiated under blue light sourced from blue LED strips (40 mW/cm^2 at 460 nm). After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using hexane/ethyl acetate as solvent system.

***1,1-Di(1H-indol-3-yl)octan-2-one (1)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 1-octyne (66.7 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 77:23) as solid (205 mg, 67%), mp (159-161 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (brs, 2H), 7.55 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 6.4 Hz, 2H), 7.12 – 7.07

(m, 4H), 5.58 (s, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.62–1.53 (m, 4H), 1.24–1.15 (m, 4H), 0.82 (t, *J* = 6.9 Hz, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 209.3, 136.4, 126.9, 123.4, 122.2, 119.7, 119.1, 113.8, 111.3, 47.1, 41.7, 31.6, 28.8, 24.2, 22.5, 14.0. IR($CHCl_3$ cm^{-1}) *v*; 3389, 3057, 2917, 2850, 1700, 1456, 1415, 1336; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{27}N_2O$ 359.2118; found: 359.2115.

***1,1-Di(1H-indol-3-yl)heptan-2-one (2)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 1-heptyne (0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (179 mg, 61%), mp (152-154 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.05 (brs, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21–7.17 (m, 2H), 7.12–7.07 (m, 2H), 7.01 (d, *J* = 2.2 Hz, 2H), 5.58 (s, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.66-1.59 (m, 2H), 1.28–1.18 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 209.1, 136.4, 126.9, 123.5, 122.2, 119.7, 119.1, 113.7, 111.3, 47.1, 41.6, 31.3, 23.6, 22.4, 13.9. IR($CHCl_3$ cm^{-1}) *v*; 3392, 2916, 1703, 1455, 1236; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{23}H_{25}N_2O$ 345.1961; found: 345.1958.

***1,1-Di(1H-indol-3-yl)hexan-2-one (3)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 1-hexyne (49.8 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (206 mg, 73%), mp (145-147 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.07 (brs, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 2.3 Hz, 2H), 5.59 (s, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 1.65 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.39–1.09 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 209.2, 136.4, 126.9, 123.4, 122.2, 119.7, 119.1, 113.8, 111.3, 47.1, 41.4, 26.4, 22.3, 13.8. IR($CHCl_3$ cm^{-1}) *v*; 3406, 2929, 1705, 1457, 1215; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{22}H_{22}N_2NaO$ 353.1624; found: 353.1623 .

***1,1-Di(1H-indol-3-yl)pentan-2-one (4)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 1-pentyne (48.2 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatog-

raphy (hexane:EA :: 75:25) as solid (189 mg, 70%), mp (138-141 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (brs, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 2.3 Hz, 2H), 5.60 (s,1H), 2.69 (t, *J* = 7.4 Hz, 2H), 1.65–1.51 (m, 1H), 1.29-1.23 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 209.0, 136.4, 126.9, 123.4, 122.2, 119.7, 119.1, 113.8, 111.3, 47.1, 43.6, 17.7, 13.7. IR($CHCl_3$ cm^{-1}) *v*; 3412, 2849, 2917, 1700, 1643, 1457, 1306, 743; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{21}N_2O$ 317.1648; found: 317.1642 .

***1-Cyclopropyl-2,2-di(1H-indol-3-yl) ethanone (5)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), cyclopropylacetylene (40.1 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 78:22) as solid (158 mg, 59%), mp (158-161 °C).^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (brs, 1H), 8.03 (brs, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.23-7.16 (m, 2H), 7.12-7.03 (m, 2H), 6.99 (d, *J* = 2.1 Hz, 2H), 5.69 (s, 1H), 2.34–2.09 (m, 1H), 1.23–1.03 (m, 2H), 0.90–0.78 (m, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 209.3, 136.4, 127.0, 123.5, 122.2, 119.6, 119.2, 113.7, 111.3, 48.2, 20.1, 11.8. IR($CHCl_3$ cm^{-1}) *v*; 3414, 2924, 2275, 1682, 1455, 1218; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{19}N_2O$ 315.1492; found: 315.1484.

***1,1-Bis(5-fluoro-1H-indol-3-yl)octan-2-one (6)*:** The title compound was prepared according to the general procedure by taking 5-fluoroindole (100 mg, 0.73 mmol), 1-octyne (57.3 µl, 0.36 mmol), thiophenol (8.0 µl, 0.073 mmol), TFA (5.6 µl, 0.073 mmol), $Ru(bpy)_3Cl_2$ (10.9 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (195 mg, 67%), mp (134-137 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (brs, 2H), 7.21 (dd, *J* = 8.8, 4.3 Hz, 2H), 7.15 (d, *J* = 2.5Hz, 1H), 7.12(d, *J* = 2.5Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 2H), 6.97-6.85 (m, 2H), 5.41 (s, 1H), 2.65 (t, *J* = 7.4 Hz, 2H), 1.65–1.51 (m, 2H), 1.24–1.14 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 209.2, 157.8 (d, *J* = 233.8 Hz), 132.9, δ = 127.0 (d, *J* = 10 Hz), 125.2, 113.3 (d, *J* = 5 Hz), 112.1 (d, *J* = 10 Hz), 110.7 (d, *J* = 26.2 Hz), 104.1 (d, *J* = 23.8 Hz), 47.2, 41.7, 31.5, 28.8, 24.2, 22.5, 14.0. IR($CHCl_3$

cm^{-1}) *v*; 3417, 2927, 2955, 1707, 1348, 1169; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{25}F_2N_2O$ 395.1929; found: 395.1927.

***1,1-Bis(5-chloro-1H-indol-3-yl)octan-2-one (7)*:** The title compound was prepared according to the general procedure by taking 5-chloroindole (100 mg, 0.65 mmol), 1-octyne (51.1 µl, 0.32 mmol), thiophenol (7.1 µl, 0.065 mmol), TFA (5 µl, 0.065 mmol), $Ru(bpy)_3Cl_2$ (9.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (177 mg, 63%), mp (140-142 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (brs, 2H), 7.47 (d, *J* = 1.9 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 2H), 5.44 (s, 1H), 2.65 (t, *J* = 7.4 Hz, 2H), 1.72–1.38 (m, 2H), 1.29–1.15 (m, 6H), 0.83 (t, *J* = 6.8 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 208.8, 134.7, 127.7, 125.5, 124.8, 122.7, 118.6, 113.1, 112.4, 46.9, 41.8, 31.6, 28.8, 24.2, 22.5, 14.0. IR($CHCl_3$ cm^{-1}) *v*; 3351, 2928, 1705, 1463, 798; HRMS (ESI) (m/z): $[M+NH_4]^+$ calculated for $C_{24}H_{28}Cl_2N_3O$ 444.1604; found: 444.1605.

***1,1-Bis(5-bromo-1H-indol-3-yl)octan-2-one (8)*:** The title compound was prepared according to the general procedure by taking 5- bromoindole (100 mg, 0.51 mmol), 1-octyne (40 µl, 0.25 mmol), thiophenol (5.6 µl, 0.051 mmol), TFA (3.9 µl, 0.051 mmol), $Ru(bpy)_3Cl_2$ (7.6 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (188 mg, 72%), mp (148-150 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (brs, 2H), 7.61 (s, 2H), 7.24 (d, *J* = 9.8 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.95 (s, 2H), 5.42 (s, 1H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.79-1.44 (m, 2H), 1.28–1.16 (m, 6H), 0.83 (t, *J* = 6.8 Hz, 3H) ; ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 209.1, 135.0, 128.4, 125.2, 124.7, 121.6, 113.1, 112.9, 112.8, 46.9, 41.8, 31.6, 28.8, 24.2, 22.5, 14.1. IR($CHCl_3$ cm^{-1}) *v*; 3362, 2922, 1704, 1461, 1218, 582; HRMS (ESI) (m/z): $[M+NH_4]^+$ calculated for $C_{24}H_{28}{}^{81}Br\,{}^{79}Br\,N_3O$ 534.0573; found: 534.0573.

***3,3'-(2-Oxooctane-1,1-diyl)bis(1H-indole-5-carbonitrile) (9)*:** The title compound was prepared according to the general procedure by taking indole-5-carbonitrile (100 mg, 0.70 mmol), 1-octyne (55 µl, 0.35 mmol), thiophenol (7.7 µl, 0.070 mmol), TFA (5.39 µl, 0.070 mmol), $Ru(bpy)_3Cl_2$ (10.4 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 72:28) as solid (186 mg, 65%), mp (150-152 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (brs, 2H), 7.82 (s, 2H), 7.43–7.37 (m, 4H), 7.28 (d, *J* =

2.2 Hz, 2H), 5.54 (s, 1H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.62-1.53 (m, 2H), 1.25–1.14 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 208.4, 138.2, 126.4, 125.6, 125.3, 125.0, 120.7, 113.7, 112.5, 102.8, 46.9, 42.0, 31.5, 28.7, 24.0, 22.5, 14.0. IR($CHCl_3$ cm^{-1}) *v*; 3330, 2918, 2850, 2222, 1708, 1653, 1248; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{26}H_{25}N_4O$ 409.2023; found: 409.2018.

***1,1-Bis(5-nitro-1H-indol-3-yl)octan-2-one (10)*:** The title compound was prepared according to the general procedure by taking 5-nitroindole (100 mg, 0.6 mmol), 1-octyne (47.9 µl, 0.3 mmol), thiophenol (6.7 µl, 0.06 mmol), TFA (4.69 µl, 0.06 mmol), $Ru(bpy)_3Cl_2$ (9.1 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 72:28) as solid (160 mg, 58%), mp (200-202 °C). ^1H NMR (400 MHz, CD_3OD) δ = 8.37 (d, *J* = 2.1 Hz, 2H), 8.02–7.82 (m, 3H), 7.40–7.36 (m, 2H), 7.30 (s, 1H), 5.74 (s, 1H), 2.64 (t, *J* = 7.1 Hz, 2H), 1.50 – 1.45 (m, 2H), 1.09–0.96 (m, 6H), 0.68 (t, *J* = 6.9 Hz, 3H); $^{13}C\{1H\}$ NMR (125 MHz, CD_3OD) δ = 209.4, 141.1, 140.0, 127.2, 125.9, 117.4, 116.3, 114.6, 111.7, 46.9, 41.7, 31.4, 28.6, 24.0, 22.3, 13.7. IR($CHCl_3$ cm^{-1}) *v*; 3347, 2918, 1701, 1623, 1518, 1331; HRMS (ESI) (m/z): $[M+NH_4]^+$ calculated for $C_{24}H_{28}N_5O_5$ 466.2085; found:466.2073.

***1,1-Bis(5-bromo-1H-indol-3-yl)pentan-2-one (11)*:** The title compound was prepared according to the general procedure by taking 5-bromoindole (100 mg, 0.5 mmol), 1-pentyne (28.9 µl, 0.25 mmol), thiophenol (5.6 µl, 0.05 mmol), TFA (3.9 µl, 0.05 mmol), $Ru(bpy)_3Cl_2$ (7.6 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 78:22) as solid (168 mg, 70%), mp (174-176 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.19 (brs, 2H), 7.63 (d, *J* = 1.6 Hz, 2H), 7.28–7.24 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 2.1 Hz, 2H), 5.43 (s, 1H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.69–1.59 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 208.7, 135.0, 128.4, 125.2, 124.6, 121.6, 113.1, 112.9, 112.9, 46.8, 43.7, 17.6, 13.7. IR($CHCl_3$ cm^{-1}) *v*; 3347, 2926, 1706, 1461, 583; HRMS (ESI) (m/z): $[M+NH_4]^+$ calculated for $C_{21}H_{22}{}^{81}Br\,{}^{79}BrN_3O$ 492.0104; found: 492.0094.

***2,2-Di(1H-indol-3-yl)-1-phenylethan-1-one (12)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), phenylacetylene (48.2 µl, 0.4 mmol), thiophenol (9.3 µl, 0.08 mmol), TFA (6.5 µl, 0.08 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 72:28) as solid (215 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$) δ =

8.12 (d, *J* = 7.2 Hz, 2H), 8.06 (brs, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 6.6 Hz, 2H), 6.99 (d, *J* = 2.3 Hz, 2H), 6.53 (s, 1H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.6, 136.9, 136.5, 132.9, 128.8, 128.6, 126.6, 124.0, 122.2, 119.7, 119.0, 114.3, 111.3, 42.1. HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{24}H_{18}N_2NaO$ 373.1311; found: 373.1300. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[9a]

***1-(4-Fluorophenyl)-2,2-di(1H-indol-3-yl)ethan-1-one (13)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 4-fluorophenylacetylene (51 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (245 mg, 78%), mp (204-207 °C). ^1H NMR (400 MHz, $CDCl_3$ and CD_3OD) δ = 8.16–8.07 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.18–7.09 (m, 2H), 7.08–6.99 (m, 4H), 6.94 (s, 2H), 6.48 (s, 1H); $^{13}C\{1H\}$ NMR (100 MHz, CD_3OD and $CDCl_3$) δ = 202.0, 169.2 (d, *J* = 296 Hz), 140.7 (d, *J* = 15 Hz), 137.2, 135.3 (d, *J* = 9 Hz), 130.4, 128.2 (d, *J* = 16 Hz), 125.7, 123.1, 122.5, 119.5 (d, *J* = 22 Hz), 117.2, 115.4 (d, *J* = 6 Hz), 46.3. IR($CHCl_3$ cm^{-1}) *v*; 3400, 3058, 2917, 1679, 1457, 1338, 1216; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{18}FN_2O$ 369.1398; found: 369.1398 .

***2,2-Di(1H-indol-3-yl)-1-(4-methoxyphenyl)ethan-1-one (14)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 4-methoxyphenylacetylene (56.16 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 72:28) as solid (224 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.15–8.10 (m, 2H), 8.04 (brs, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 5.8 Hz, 2H), 6.97 (d, *J* = 2.3 Hz, 2H), 6.92–6.86 (m, 2H), 6.49 (s, 1H), 3.85 (s, 3H); $^{13}C\{1H\}$ NMR (100MHz, $CDCl_3$) δ = 197.1, 163.4, 136.6, 131.1, 129.9, 126.8, 123.9, 122.2, 119.7, 119.0, 114.7, 113.8, 111.3, 55.4, 41.7. HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{25}H_{20}N_2NaO_2$ 403.1417; found: 403.1415. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[9a]

***1-(4-(Tert-butyl)phenyl)-2,2-di(1H-indol-3-yl)ethan-1-one (15)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 4-*tert*-butylphenylacetylene (84 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 71:29) as solid (260 mg, 75%), mp (153-155 °C). ^{1}H NMR (400 MHz, $CDCl_3$ and CD_3OD) δ = 8.06 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.48–7.30 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.97 (s, 2H), 6.54 (s, 1H), 1.31 (s, 9H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$ and CD_3OD) δ = 199.3, 156.7, 136.6, 134.1, 128.7, 126.6, 125.5, 124.2, 121.7, 119.1, 118.7, 113.6, 111.3, 42.0, 35.0, 30.9. IR($CHCl_3$ cm^{-1}) *v*; 3330, 2921, 2957, 2851, 1695, 1642, 1336; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{28}H_{26}N_2NaO$ 429.1937; found: 429.1934 .

***1-(4-Ethylphenyl)-2,2-di(1H-indol-3-yl)ethan-1-one (16)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), 4-ethylphenylacetylene (61.5µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (223 mg, 69%), mp (142-149 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.3 Hz, 4H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.19–7.14 (m, 2H), 7.09–7.04 (m, 2H), 6.94 (d, *J* = 2.1 Hz, 2H), 6.50 (s, 1H), 2.68 (q, *J* =7.4 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 198.2, 149.8, 136.5, 134.6, 129.0, 128.1, 126.7, 124.0, 122.2, 119.6, 119.0, 114.5, 111.3, 41.9, 28.9, 15.1. IR($CHCl_3$ cm^{-1}) *v*; 3403, 2956, 1667, 1457; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{26}H_{22}N_2NaO$ 401.1624; found: 401.1612.

***2,2-Di(1H-indol-3-yl)-1-(p-tolyl)ethan-1-one (17)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), p-tolylacetylene (54.8 µl, 0.4 mmol), thiophenol (9.3 µl, 0.085 mmol), TFA (6.5 µl, 0.085 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (220 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (brs, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.13 (m, 4H), 7.06 (t, *J* = 7.1 Hz, 2H), 6.96 (d, *J* = 2.1 Hz, 2H), 6.49 (s, 1H), 2.36 (s, 3H); ^{13}C{1H} NMR

(125 MHz, DMSO-d_6) δ = 198.0, 143.7, 136.8, 134.5, 129.7, 129.1, 126.9, 124.8, 121.5, 119.4, 118.9, 113.5, 112.0, 41.8, 21.5. HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{25}H_{20}N_2NaO$ 387.1468; found: 387.1461. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[9a]

***2,2-Bis(6-chloro-1H-indol-3-yl)-1-phenylethanone (18)*:** The title compound was prepared according to the general procedure by taking 6-chloroindole (100 mg, 0.65 mmol), phenylacetylene (36.9 µl, 0.3 mmol), thiophenol (7.1 µl, 0.065 mmol), TFA (5 µl, 0.065 mmol), $Ru(bpy)_3Cl_2$ (9.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 77:23) as solid (201 mg, 73%), mp (138-140 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.12 (brs, 2H), 8.09-8.05 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45-7.39 (m, 4H), 7.30 (s, 2H), 7.03 (dd, *J* = 8.5, 1.6 Hz, 2H), 6.89 (s, 2H), 6.41 (s, 1H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.3, 136.8, 136.6, 133.2, 128.8, 128.8, 128.3, 125.1, 124.6, 120.6, 119.8, 114.1, 111.4, 42.0. IR($CHCl_3$ cm^{-1}) *v*; 3424, 2922, 1674, 1460, 1226, 770; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{17}Cl_2N_2O$ 419.0712; found: 419.0707.

***2,2-Bis(5-fluoro-1H-indol-3-yl)-1-phenylethan-1-one (19)*:** The title compound was prepared according to the general procedure by taking 5-fluoroindole (100 mg, 0.73 mmol), phenylacetylene (41.4 µl, 0.36 mmol), thiophenol (8.0 µl, 0.073 mmol), TFA (5.6 µl, 0.073 mmol), $Ru(bpy)_3Cl_2$ (10.9 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (217 mg, 76%), mp (144-148 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.16–8.06 (m, 4H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.27–7.22 (m, 2H), 7.18 (dd, *J* = 9.6, 2.3 Hz, 2H), 7.03 (d, *J* = 2.2 Hz, 2H), 6.96-6.91 (m, 2H), 6.37 (s, 1H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.2, 157.9 (d, *J* = 233.8 Hz), 136.5, 133.5, 133.1 (d, *J* = 26.2 Hz), 128.8 (d, *J* = 7.5 Hz), 126.9 (d, *J* = 10 Hz), 125.6, 125.4, 114.1 (d, *J* = 4.6 Hz), 112.0 (d, *J* = 10 Hz), 110.8 (d, *J* = 26.2 Hz), 104.0, (d, *J* = 23.7 Hz),42.1. IR($CHCl_3$ cm^{-1}) *v*; 3354, 2923, 2852, 1677, 1485, 1216, 1181; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{24}H_{16}F_2N_2NaO$ 409.1123; found: 409.1121.

***2,2-Bis(5-chloro-1H-indol-3-yl)-1-phenylethan-1-one (20)*:** The title compound was prepared according to the general procedure by taking 5-chloroindole (100 mg, 0.65 mmol), phenylacetylene (36.9 µl,

0.3 mmol), thiophenol (7.1 µl, 0.065 mmol), TFA (5 µl, 0.065 mmol), $Ru(bpy)_3Cl_2$ (9.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (196 mg, 71%), mp (132-134 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (brs, 2H), 8.08 (d, *J* = 1.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.11 (dd, *J* = 8.6, 1.9 Hz, 2H), 6.84 (d, *J* = 2.4 Hz, 2H), 6.38 (s, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 198.5, 136.4, 134.9, 133.4, 128.9, 128.8, 127.5, 125.5, 125.4, 122.7, 118.3, 113.4, 112.5, 42.1. IR($CHCl_3$ cm^{-1}) *v*; 3429, 1677, 1462, 1216, 762; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{24}H_{16}Cl_2N_2NaO$ 441.0532; found: 441.0518.

***2,2-Bis(5-bromo-1H-indol-3-yl)-1-phenylethan-1-one (21)*:** The title compound was prepared according to the general procedure by taking 5-bromoindole (100 mg, 0.51 mmol), phenylacetylene (28.9 µl, 0.25 mmol), thiophenol (5.6 µl, 0.051 mmol), TFA (3.9 µl, 0.051 mmol), $Ru(bpy)_3Cl_2$ (7.6mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (178 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (brs, 2H), 8.13-8.05 (m, 2H), 7.67 (s, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.28-7.23 (m, 2H), 7.22-7.17 (m, 2H), 6.94 (s, 2H), 6.38 (s, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 197.9, 136.4, 135.2, 133.2, 128.8, 128.8, 128.2, 125.3, 125.1, 121.5, 113.6, 113.2, 112.9, 42.0. HRMS (ESI) (m/z): $[M-H]^-$calculated for $C_{24}H_{15}Br^{79}Br^{81}N_2O$ 506.9531; found: 506.9528. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[9d]

***2,2-Bis(5-iodo-1H-indol-3-yl)-1-phenylethan-1-one (22)*:** The title compound was prepared according to the general procedure by taking 5-iodoindole (100 mg, 0.41 mmol), phenylacetylene (23.3 µl, 0.2 mmol) , thiophenol (4.5 µl, 0.04 mmol), TFA (3.2 µl, 0.04 mmol), $Ru(bpy)_3Cl_2$ (6.1 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 74:26) as solid (173 mg, 70%), mp (156-158 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (brs, 2H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.83 (s, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46–7.36 (m, 4H), 7.13–6.92 (m, 2H), 6.71 (s, 2H), 6.33 (s, 1H); ^{13}C {1H} NMR (125 MHz,$CDCl_3$ and CD_3OD) δ = 199.1, 136.3, 135.8, 133.2, 130.1, 129.0, 128.8, 128.7, 127.3, 125.1,

113.6, 112.4, 82.6, 42.1. IR($CHCl_3$ cm^{-1}) *v*; 3418, 2924, 1674, 1454, 1215; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{17}I_2N_2O$ 602.9425; found: 602.9422.

***3,3'-(2-Oxo-2-phenylethane-1,1-diyl)bis(1H-indole-5-carbonitrile) (23)*:** The title compound was prepared according to the general procedure by taking indole-5-carbonitrile (100 mg, 0.70 mmol), phenylacetylene (39.7 µl, 0.35 mmol), thiophenol (7.7 µl, 0.07 mmol), TFA (5.4 µl, 0.07 mmol), $Ru(bpy)_3Cl_2$ (10.4 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 72:28) as solid (188 mg, 67%), mp (192-194 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.66 (brs, 2H), 8.12–8.07 (m, 2H), 7.88 (s, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 0.9 Hz, 4H), 7.18 (d, *J* = 2.4 Hz, 2H), 6.49 (s, 1H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 197.6, 138.3, 136.0, 133.7, 129.0, 128.8, 126.3, 125.9, 125.4, 125.0, 120.6, 114.4, 112.5, 103.0, 41.9. IR($CHCl_3$ cm^{-1}) *v*; 3331, 2923, 2223, 1669, 1446, 1217; HRMS (ESI) (m/z): $[M+NH_4]^+$ calculated for $C_{26}H_{20}N_5O$ 418.1662; found: 418.1666.

***2,2-Bis(5-nitro-1H-indol-3-yl)-1-phenylethan-1-one (24)*:** The title compound was prepared according to the general procedure described as above by taking 5-nitroindole (100 mg, 0.6 mmol), phenylacetylene (34.6 µl, 0.3 mmol), thiophenol (6.7 µl, 0.06 mmol), TFA (4.7 µl, 0.06 mmol), $Ru(bpy)_3Cl_2$ (9.1 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 70:30) as solid (171 mg, 63%), mp (252-254 °C). ^1H NMR (400 MHz, $CDCl_3$ and CD_3OD) δ = 8.42 (s, 2H), 8.10–7.86 (m, 4H), 7.54–7.45 (m, 1H), 7.43–7.31 (m, 4H), 7.29–7.26 (m, 1H), 7.17 (s, 1H), 6.51 (s, 1H); $^{13}C\{1H\}$ NMR (125 MHz, Acetone-d_6) δ = 197.3, 141.4, 140.0, 136.6, 133.2, 128.9, 128.7, 128.1, 126.2, 116.9, 116.5, 116.1, 111.9, 41.6. IR($CHCl_3$ cm^{-1}) *v*; 3432, 2923, 1653, 1520, 1468, 1336; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{17}N_4O_5$ 441.1193; found: 441.1192 .

***2,2-Bis(2-methyl-1H-indol-3-yl)-1-phenylethan-1-one (25)*:** The title compound was prepared according to the general procedure by taking 2-methylindole (100 mg, 0.76 mmol), phenylacetylene (43.1 µl, 0.38 mmol), thiophenol (8.3 µl, 0.076 mmol), TFA (5.6 µl, 0.076 mmol), $Ru(bpy)_3Cl_2$ (11.4 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 78:22) as solid (204 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.10–8.05 (m, 2H), 7.82 (brs, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42–7.32 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.98 (t, *J* = 6.8 Hz, 2H), 6.43 (s, 1H), 2.17 (s, 6H);

$^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 198.8, 137.2, 135.0, 132.8, 132.4, 128.7, 128.6, 128.5, 121.0, 119.5, 118.5, 110.2, 108.8, 42.8, 12.6. HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{26}H_{22}N_2NaO$ 401.1624; found: 401.1623. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[9a]

***2,2-Di(1H-indol-3-yl)-1,2-diphenylethan-1-one (26)*:** The title compound was prepared according to the general procedure by taking indole (100 mg, 0.85 mmol), diphenylacetylene (75.7 mg, 0.4 mmol), thiophenol (9.3 µl, 0.08 mmol), TFA (6.5 µl, 0.08 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 80:20) as solid (265 mg, 73%), mp (192-194 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.02 (brs, 2H), 7.89–7.82 (m, 2H), 7.36 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.27–7.22 (m, 4H), 7.22–7.15 (m, 2H), 7.12–7.04 (m, 4H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.88 (d, *J* = 2.5 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 2H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 199.1, 142.6, 138.3, 136.5, 131.7, 130.7, 130.1, 127.6, 127.5, 127.4, 126.5, 124.5, 121.9, 121.9, 119.5, 119.0, 111.0, 61.1. IR($CHCl_3$ cm^{-1}) *v*; 3408, 2917, 2849, 1755, 1746, 1453, 1359, 1208; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{30}H_{22}N_2NaO$ 449.1624; found: 449.1620 . The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[23]

***2,2-Di(1H-indol-3-yl)-1-phenylpropan-1-one (27)*:** The title compound was prepared according to the general procedure described as above by taking indole (100 mg, 0.85 mmol), 1-phenyl-1-propyne (54.8 µl, 0.4 mmol), thiophenol (9.3 µl, 0.08 mmol), TFA (6.5 µl, 0.08 mmol), $Ru(bpy)_3Cl_2$ (12.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 79:21) as solid (214 mg, 69%), mp (132-134 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.06 (brs, 2H), 7.75–7.71 (m, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.20–7.14 (m, 4H), 7.07–7.02 (m, 2H), 6.94 (d, *J* = 2.5 Hz, 2H), 2.20 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 202.6, 138.4, 136.9, 131.2, 129.4, 127.6, 126.2, 123.2, 122.0, 121.6, 119.8, 119.5, 111.3, 51.8, 26.6. IR($CHCl_3$ cm^{-1}) *v*; 3405, 2919, 2850, 1688, 1619, 1240; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{25}H_{20}N_2NaO$ 387.1468; found: 387.1464.

***2,2-Bis(5-fluoro-1H-indol-3-yl)-1,2-diphenylethanone (28)*:** The title compound was prepared according to the general procedure by taking 6-fluoroindole (100 mg, 0.73 mmol), diphenylacetylene (65 mg, 0.36 mmol), thiophenol (8.0 µl, 0.073 mmol), TFA (5.6 µl, 0.073 mmol), $Ru(bpy)_3Cl_2$ (10.9 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (243 mg, 71%), mp (133-135 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (brs, 2H), 7.87–7.81 (m, 2H), 7.39–7.34 (m, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.27–7.23 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 2H), 6.96 – 6.91 (m, 4H), 6.84 (s, 2H), 6.61–6.54 (m, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 199.0, 159.6 (d, *J* = 236.2 Hz),142.1, 137.8, 136.3 (d, *J* = 12.4 Hz), 132.1, 130.7, 129.8, 127.8 (d, *J* = 36.2 Hz) , 126.9, 124.6, 124.6, 123.9, 122.4 (d, *J* = 10 Hz), 119.1, 108.4 (d, *J* = 23.8 Hz), 97.2 (d, *J* = 26.2 Hz), 60.9. IR($CHCl_3$ cm^{-1}) *v*; 3370, 2926, 1627, 1446, 1217; HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{30}H_{19}F_2N_2O$ 461.1471; found: 461.1499.

***2,2-Bis(5-chloro-1H-indol-3-yl)-1,2-diphenylethanone (29)*:** The title compound was prepared according to the general procedure by taking 5-chloroindole (100 mg, 0.65 mmol), diphenylacetylene (57.9 mg, 0.32 mmol), thiophenol (7.1 µl, 0.065 mmol), TFA (5 µl, 0.065 mmol), $Ru(bpy)_3Cl_2$ (9.7 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (238 mg, 73%), mp (152-154 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (brs, 2H), 7.82–7.79 (m, 2H), 7.37–7.32 (m, 3H), 7.27–7.24 (m, 3H), 7.18–7.13 (m, 4H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.95 (s, 3H), 6.83 (d, *J* = 2.6 Hz, 2H); ^{13}C{1H} NMR (125MHz, $CDCl_3$) δ = 198.5, 141.4, 137.5, 134.9, 132.1, 130.8, 129.6, 128.3, 128.2, 127.8, 127.1, 125.7, 125.1, 122.5, 120.9, 118.5, 112.2, 60.9. IR($CHCl_3$ cm^{-1}) *v*; 3421, 3421, 2928, 1603, 1217, 749; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{30}H_{20}Cl_2N_2NaO$ 517.0839; found: 517.0815.

***2,2-Bis(5-bromo-1H-indol-3-yl)-1,2-diphenylethanone (30)*:** The title compound was prepared according to the general procedure by taking 5-bromoindole (100 mg, 0.51 mmol), diphenylacetylene (45 mg, 0.25 mmol), thiophenol (5.6 µl, 0.051 mmol), TFA (3.92 µl, 10 mol%), $Ru(bpy)_3Cl_2$ (7.6 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (222 mg, 75%), mp (168-171 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (brs, 2H), 7.81–7.77 (m, 2H), 7.36–7.30 (m, 3H), 7.28–7.23 (m, 4H), 7.15 (t, *J* = 7.8 Hz, 2H), 7.10 (s, 2H), 7.08 (s, 3H), 6.78 (d, *J* = 2.6 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 198.6, 141.4, 137.5, 135.2, 132.2, 130.8, 129.6, 128.9, 128.2, 127.8, 127.1,

125.6, 125.0, 123.9, 118.3, 112.8, 112.7,60.9. IR($CHCl_3$ cm^{-1}) *v*; 3416, 2926, 1668, 1446, 1216, 582; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{30}H_{21}Br_2N_2O$ 583.0015; found: 583.0019.

***2,2-Bis(5-nitro-1H-indol-3-yl)-1,2-diphenylethanone (31)*:** The title compound was prepared according to the general procedure by taking 5-nitroindole (100 mg, 0.6 mmol), diphenylacetylne (54.3 mg, 0.3 mmol) , thiophenol (6.7 µl, 0.06 mmol), TFA (4.7 µl, 0.06 mmol), $Ru(bpy)_3Cl_2$ (9.1 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 66:34) as solid (197 mg, 62%), mp (197-200 °C). ^1H NMR (400 MHz, CD_3OD) δ = 8.43 (d, *J* = 2.3 Hz, 1H), 8.37 (dd, *J* = 9.3, 2.3 Hz, 1H), 8.34 (d, *J* = 2.4 Hz, 1H), 8.26 (d, *J* = 2.1 Hz, 1H), 8.20 (d, *J* = 2.1 Hz, 2H), 7.98–7.87 (m, 4H), 7.49–7.26 (m, 6H), 7.08–6.94 (m, 2H); $^{13}C\{1H\}$ NMR (125 MHz, CD_3OD) δ = 199.1, 162.8, 141.2, 140.6, 139.2, 132.9, 127.0, 126.7, 126.0, 124.6, 122.2, 120.1, 116.2, 115.3, 111.7, 111.3, 111.2, 68.8. IR($CHCl_3$ cm^{-1}) *v*; 3422, 3023, 1647, 1335, 1216; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{30}H_{21}N_4O_5$ 517.1506; found: 517.1522.

***2-(1H-Indol-3-yl)-2-(2-methyl-1H-indol-3-yl)-1-phenylethan-1-one (32)*:** The title compound was prepared according to the general procedure by taking 2-methylindole (100 mg, 0.76 mmol), indole (88.92 mg, 0.76 mmol), phenylacetylene (86.24 µl, 0.38 mmol) , thiophenol (8.3 µl, 0.076 mmol), TFA (5.8 µl, 0.076 mmol), $Ru(bpy)_3Cl_2$ (11.4 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 76:24) as solid (94 mg, 34%), mp (160-162 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.4 Hz, 2H), 7.99 (s, 1H), 7.86 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43–7.33 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.19–7.09 (m, 2H), 7.09–7.02 (m, 2H), 6.84 (d, *J* = 1.6 Hz, 1H), 6.40 (s, 1H), 2.34 (s, 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 198.2, 137.2, 136.5, 135.2, 132.7,132.7, 128.6, 128.5, 128.1, 127.0, 124.1, 122.1, 121.2, 119.7, 119.6, 119.0, 118.9, 114.4, 111.3, 110.3, 108.2, 42.2, 12.4. IR($CHCl_3$ cm^{-1}) *v*; 3396, 2849, 2917, 1680, 1459, 1306; HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{25}H_{20}N_2NaO$ 387.1473; found: 387.1467. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[9c]

***2-(5-Fluoro-1H-indol-3-yl)-2-(2-methyl-1H-indol-3-yl)-1-phenylethan-1-one (33)*:** The title compound was prepared according to the general procedure by taking 2-methylindole (100 mg, 0.76 mmol),

5-fluoroindole (102.7 mg , 0.76 mmol), phenylacetylene (86.2 µl, 0.38 mmol) , thiophenol (8.3 µl, 0.076 mmol), TFA (5.8 µl, 0.076 mmol), $Ru(bpy)_3Cl_2$ (11.4 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (110 mg, 38%), mp (168-169 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 1.3 Hz, 2H), 8.02 (s, 1H), 7.90 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 15.5, 7.3 Hz, 1H), 7.13–7.00 (m, 4H), 6.87 (t, *J* = 9.1 Hz, 1H), 6.79 (s, 1H), 6.30 (s, 1H), 2.32 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 198.0, 157.7 (d, *J* = 233.8 Hz), 136.9, 135.2, 133.0, 132.9, 132.7, 128.6, 127.9, 127.1 (d, *J* = 10 Hz), 126.0, 121.3, 119.7, 118.8, 114.4 (d, *J* = 3.8 Hz), 112.0 (d, *J* = 10 Hz), 110.4, 110.4, 110.2, 107.9, 103.9 (d, *J* = 23.7 Hz), 42.3, 12.3. IR($CHCl_3$ cm^{-1}) *v*; 3393, 2919, 1679, 1454, 1316, 1184; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{25}H_{20}FN_2O$ 383.1554; found: 383.1561.

***2-(5-Bromo-1H-indol-3-yl)-2-(2-methyl-1H-indol-3-yl)-1-phenylethan-1-one (34)*:** The title compound was prepared according to the general procedure by taking 2-methylindole (100 mg, 0.76 mmol), 5-bromoindole (148.9 mg, 0.76 mmol), phenylacetylene (86.2 µl, 0.38 mmol) , thiophenol (8.3 µl, 0.076 mmol), TFA (5.8 µl, 0.076 mmol), $Ru(bpy)_3Cl_2$ (11.4 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 75:25) as solid (138 mg, 41%), mp (170-172 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 7.3 Hz, 3H), 7.89 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.53–7.45 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 10.7 Hz, 2H), 7.19–6.97 (m, 3H), 6.81 (s, 1H), 6.30 (s, 1H), 2.36 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 197.8, 136.8, 135.2, 135.2, 132.9, 132.5, 128.6, 128.6, 127.9, 125.5, 124.9, 121.5, 121.3, 119.8, 118.8, 114.1, 112.8, 112.8, 110.4, 108.0, 42.2, 12.4. IR($CHCl_3$ cm^{-1}) *v*; 3400.0, 2923.3, 1677.2, 1459.5, 1216.3, 584.2; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{25}H_{20}BrN_2O$ 443.0754; found: 443.0736. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[9c]

***Methyl 1-heptanoyl-9H-pyrido[3,4-b]indole-3-carboxylate (47)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 1-octyne (70.8 µl, 0.45 mmol), thiophenol (4.9 µl, 0.045 mmol), TFA (34.6 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as solid (111 mg, 72%), mp (162-

166 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.51 (brs, 1H), 9.00 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.66–7.52 (m, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 4.06 (s, 3H), 3.46 (t, *J* = 7.4 Hz, 2H), 1.87–1.75 (m, 2H), 1.49–1.23 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 205.5, 166.2, 141.4, 136.8, 136.5, 135.1, 131.9, 129.7, 122.1, 121.6,121.0, 121.2, 112.3, 52.8, 37.5, 31.8, 29.1, 24.1, 22.6, 14.1. IR($CHCl_3$ cm^{-1}) *v*; 3364, 2928, 1720, 1360, 1260; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{23}N_2O_3$ 339.1703; found: 339.1699.

***Methyl 1-hexanoyl-9H-pyrido[3,4-b]indole-3-carboxylate (48)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 1-heptyne (61.7 µl, 0.45 mmol), thiophenol (4.9 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as solid (102 mg, 69%), mp (156-158 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.50 (brs, 1H), 9.00 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.66–7.56 (m, 2H), 7.48-7.27(m, 1H), 4.06 (s, 3H), 3.46 (t, *J* = 7.4 Hz, 2H), 1.82 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.46–1.38 (m, 4H), 0.92 (t, *J* = 5.6 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 205.5, 166.2, 141.4, 136.7, 136.5, 135.1, 131.9, 129.7,121.0, 122.1, 121.6, 121.2, 112.3, 52.8, 37.5, 31.6, 23.8, 22.6, 14.0. IR($CHCl_3$ cm^{-1}) *v*; 3417, 2954, 2926, 1713, 1626, 1511, 1261, 1121; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{21}N_2O_3$ 325.1547; found: 325.1549.

***Methyl 1-pentanoyl-9H-pyrido[3,4-b]indole-3-carboxylate (49)*:** The title compound was prepared according to the general procedure described as above by taking tryptophan methyl ester (100 mg, 0.45 mmol), 1-hexyne (52.8 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol) , $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 98:2) as solid (100 mg, 71%), mp (145-148 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.54 (brs, 1H), 9.02 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.68–7.60 (m, 2H), 7.54–7.30 (m, 1H), 4.09 (s, 3H), 3.50 (t, *J* = 7.4 Hz, 2H), 1.89–1.77 (m, 2H), 1.56–1.42 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 205.5, 166.2, 141.4, 136.7, 136.5, 135.1, 131.9, 129.7, 122.0, 121.6, 121.2,120.8, 112.3, 52.8, 37.2, 26.2, 22.5, 14.0. IR($CHCl_3$ cm^{-1}) *v*; 3363, 2923, 1715, 1495, 1337, 1261; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{19}N_2O_3$ 311.1390; found: 311.1396.

***Methyl 1-butyryl-9H-pyrido[3,4-b]indole-3-carboxylate (50)*:**The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 1-pentyne (51.1 µl, 0.45 mmol) , thiophenol (4.9 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol) , $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as solid (92 mg, 68%), mp (194-196 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.53 (brs, 1H), 9.01 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.66–7.57 (m, 2H), 7.41–7.35 (m, 1H), 4.08 (s, 3H), 3.47 (t, *J* = 7.3 Hz, 2H), 1.93–1.83 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 205.2, 166.2, 141.4, 136.7, 136.5, 135.2, 131.8, 129.7, 122.0, 121.6, 121.1, 112.3, 53.5, 52.8, 39.4, 17.5, 13.9. IR($CHCl_3$ cm^{-1}) *v*; 3400, 2932, 2874, 1704, 1664, 1436, 1332, 1266; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{17}N_2O_3$ 297.1234; found: 297.1239.

***Methyl 1-(cyclopropanecarbonyl)-9H-pyrido[3,4-b]indole-3-carboxylate (51)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), cyclopropylacetylene (42.5 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 98:2) as solid (89 mg, 66%), mp (245-247 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.57 (brs, 1H), 9.06 (s, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 7.65–7.59 (m, 2H), 7.40 (t, *J* = 6.8 Hz, 1H), 4.10 (s, 3H), 3.94–3.88 (m, 1H), 1.41–1.36 (m, 2H), 1.30–1.18 (m, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 203.9, 166.2, 141.4, 136.8, 136.4, 135.4, 131.9, 129.7, 122.1, 121.6, 121.1, 120.9, 112.3, 52.9, 16.0, 13.6. IR($CHCl_3$ cm^{-1}) *v*; 3363, 2920, 2850, 1700, 1495, 1327, 1266; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{15}N_2O_3$ 295.1077; found: 295.1057.

***Methyl 1- benzoyl-9-H-pyrido(3,4-b)indole-3 carboxylate (52)*:** The title compound was prepared according to general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), phenylacetylene (51.9 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol) , $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 95:5) as solid (113 mg, 75%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.70 (brs, 1H), 9.06 (s, 1H), 8.63 (d, *J* = 7.4 Hz, 2H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.71–7.62 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.45–7.39 (m, 1H), 4.07 (s, 3H); ^{13}C{1H} NMR (125 MHz,

$CDCl_3$) δ = 193.8, 166.2, 141.3, 138.3, 136.8, 136.4, 135.6, 133.0, 132.1, 132.0, 129.8, 128.2, 122.1, 121.7, 121.2, 120.7, 112.4, 52.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{15}N_2O_3$ 331.1077; found: 331.1043. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[20d]

***Methyl 1-(4-fluorobenzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (53)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 4-fluoro phenylacetylene (54 µl, 0.45 mmol), thiophenol, (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as solid (114 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$) δ = 10.73 (brs, 1H), 9.11 (s, 1H), 8.90 – 8.70 (m, 2H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.71 (s, 2H), 7.48 (d, *J* = 6.3 Hz, 1H), 7.32 – 7.27 (m, 2H), 4.13 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.9, 166.1, 165.9 (d, *J* = 253.8 Hz), 141.3, 138.3, 136.3, 135.4, 134.7 (d, *J* = 8.7 Hz), 133.1, 133.0, 132.2, 129.9, 121.9 (d, *J* = 41.2 Hz), 121.2, 120.7, 115.3 (d, *J* = 21.2 Hz),112.4, 52.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{14}FN_2O_3$ 349.0983; found: 349.0946. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[20h]

***Methyl 1-(4-methoxybenzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (54)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 4-methoxy phenylacetylene (59.4 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 94:6) as solid (115 mg, 70%).^1H NMR (400 MHz, $CDCl_3$) δ = 10.71 (brs, 1H), 9.05 (s, 1H), 8.76 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 7.9 Hz, 1H), 7.75–7.58 (m, 2H), (7.46–7.38 (m, 1H), 7.07 (d, *J* = 9.0 Hz, 2H), 4.09 (s, 3H), 3.94 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 191.7, 166.3, 163.7, 141.2, 141.2, 138.3, 136.2, 136.2, 134.5, 131.9, 129.7, 122.0, 121.6, 121.2, 120.4, 113.6, 112.4, 55.5, 52.8. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{17}N_2O_4$ 361.1183; found: 361.1190. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[20d]

***Methyl 1-(4-(tert-butyl)benzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (55)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 4-*tert*- butylphenylacetylene (89 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 95:5) as solid (131 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.75 (brs, 1H), 9.06 (s, 1H), 8.65–8.60 (m, 2H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.62 – 7.59 (m, 2H), 7.47 – 7.37 (m, 1H), 4.10 (s, 3H), 1.41 (s, 9H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 193.3, 166.3, 156.8, 141.3, 138.3, 136.3, 135.8, 134.1, 132.0, 131.9, 129.8, 125.3, 122.1, 121.6, 121.1, 120.6, 112.4, 52.9,35.2, 31.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{24}H_{23}N_2O_3$ 387.1703; found: 387.1706. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[20d]

***Methyl 1-(4-propylbenzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (56)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 4n-Propyl phenylacetylene (72.1 µl, 0.45 mmol) , thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography(hexane:EA :: 96:4) as solid (136 mg, 80%), mp (157-159 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.73 (brs, 1H), 9.06 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 2H), 8.25 (d, *J* = 7.9 Hz, 1H), 7.69–7.64 (m, 2H), 7.44–7.39 (m, 2H), 7.38 (s, 1H), 4.08 (s, 3H), 2.72 (t, *J* = 7.2 Hz, 2H), 1.79–1.69 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 193.2, 166.3, 148.6, 141.3, 138.3, 136.3, 135.9, 134.4, 132.1, 132.0, 129.7, 128.4, 122.0, 121.6, 121.2, 120.5, 112.4, 52.8, 38.2, 24.3, 13.9. IR($CHCl_3$ cm^{-1}) *ν*; 3389, 2924, 1716, 1603, 1455, 1293, 1260; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{23}H_{21}N_2O_3$ 373.1547; found: 373.1543.

***Methyl 1-(4-ethylbenzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (57)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 4-ethyl phenylacetylene (65 µl, 0.45 mmol) , thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol) , $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as solid (126 mg, 77%), mp (194-196 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.69 (brs, 1H), 9.04 (s, 1H), 8.57 (d, *J* = 8.3 Hz, 2H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.71–7.56 (m, 2H), 7.45–7.31 (m, 3H), 4.06 (s, 3H), 2.75

(q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.4 Hz, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 193.3, 166.3, 150.1, 141.3, 138.3, 136.3, 135.9, 134.4, 132.2, 132.0, 129.8, 127.8, 122.1, 121.6, 121.2, 120.6, 112.4, 52.8, 29.1, 15.3. IR($CHCl_3$ cm^{-1}) v; 3363, 2958, 2851, 1714, 1495, 1359, 1260; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{22}H_{19}N_2O_3$ 359.1390; found: 359.1355.

***Methyl 1-(4-methylbenzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (58)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), p-tolyl acetylene(58 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as solid (107 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$) δ = 10.68 (brs, 1H), 9.03 (s, 1H), 8.54 (d, J = 8.2 Hz, 2H), 8.22 (d, J = 7.9 Hz, 1H), 7.72–7.60 (m, 2H), 7.44–7.30 (m, 3H), 4.05 (s, 3H), 2.45 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 193.3, 166.3, 143.9, 141.3, 138.3, 136.3, 135.9, 134.2, 132.1, 132.0, 129.8, 129.0, 122.0, 121.6, 121.2, 120.5, 112.4, 52.8, 21.8. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{17}N_2O_3$ 345.1234; found: 345.1206. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[20d]

***Methyl 1-(2-(trifluoromethyl)benzoyl)-9H-pyrido[3,4-b]indole-3-carboxylate* (59):** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 2- (trifluoromethyl)phenylacetylene (62.7 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 94:6) as solid (118 mg , 65%). ^1H NMR (400 MHz, $CDCl_3$) δ = 10.69 (brs, 1H), 9.09 (s, 1H), 8.30 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.79–7.69 (m, 4H), 7.54–7.45 (m, 1H), 4.00 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 197.4, 165.9, 141.5, 137.8, 137.1, 136.6, 134.6 (q, J = 8.8 Hz), 132.2, 130.9, 130.5,130.4, 130.0, 129.2, 128.9, 128.2, 126.8 (q, J = 17.5 Hz), 121.9, 121.6(q, J = 216.2 Hz), 119.8, 112.5, 52.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -57.6; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{14}F_3N_2O_3$ 399.0951; found: 399.0948. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[20d]

***Methyl 1-(6-methoxy-2-naphthoyl)-9H-pyrido[3,4-b]indole-3-carboxylate (60)*:** The title compound was prepared according to the general procedure by taking tryptophan methyl ester (100 mg, 0.45 mmol), 2-Ethynyl- 6-methoxynaphthalene (81.9 µl, 0.45 mmol), thiophenol (4.95 µl, 0.045 mmol), TFA (34 µl, 0.45 mmol), $Ru(bpy)_3Cl_2$ (6.8 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 93:7) as solid (146 mg, 78%), mp (239-241 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.77 (brs, 1H), 9.60 (s, 1H), 9.08 (s, 1H), 8.52 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.50 – 7.40 (m, 1H), 7.27 – 7.17 (m, 2H), 4.12 (s, 3H), 4.00 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 192.5, 166.3, 160.0, 141.3, 138.3, 137.3, 136.2, 136.1, 135.3, 132.1,132.0, 131.9, 129.8, 128.0, 127.4, 126.6, 122.1, 121.6, 121.2, 120.5, 119.4, 112.4, 105.6, 55.5, 52.9. IR($CHCl_3$ cm^{-1}) *v*; 3416, 2921, 2850, 1711, 1436, 1304, 1261; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{25}H_{19}N_2O_4$ 411.1339; found: 411.1373.

***Cyclopropyl(4,9-dihydro-3H-pyrido[3,4-b]indol-1-yl)methanone (61)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), cyclopropylacetylene (58.5 µl, 0.62 mmol), thiophenol (6.8 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as semi solid (96 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.62 (brs, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.20–4.14 (m, 2H), 3.32–3.22 (m, 1H), 3.01–2.95 (m, 2H), 1.28–1.17 (m, 1H), 1.15–1.10 (m, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 202.6, 155.4, 137.0, 126.3, 125.0, 120.7, 120.2, 119.9, 117.8, 112.2, 49.4, 19.0, 15.2, 13.1. IR($CHCl_3$ cm^{-1}) *v*; 3239, 2923, 2350, 1659, 1214; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{15}N_2O$ 239.1179; found: 239.1202.

***(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(phenyl)methanone (62)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), phenylacetylene (70.3 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as semi solid (121 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.43 (brs, 1H), 8.20 – 8.15 (m, 2H), 7.62 (t, *J* = 6.7 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.17 (t, *J* = 7.1 Hz, 1H), 4.18 (dd, *J* = 9.5,

8.1 Hz, 2H), 3.04 (dd, *J* = 9.5, 8.1 Hz, 2H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 193.4, 155.9, 137.0, 135.3, 133.6, 131.1, 128.3, 126.7, 125.2, 124.8, 120.4, 120.0, 118.1, 112.3, 49.3, 19.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{15}N_2O$ 275.1179; found: 275.1175. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[22c]

***(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(4-fluorophenyl)methanone (63)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-fluorophenylacetylene (74.4 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 95:5) as solid (136 mg, 75%), mp (122-124 °C). ^1H NMR (400 MHz, $CDCl_3$) δ = 9.42 (brs, 1H), 8.30 – 8.25 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.19 (d, *J* = 1.8 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 4.18 (dd, *J* = 9.5, 8.1 Hz, 2H), 3.03 (dd, *J* = 9.4, 8.1 Hz, 2H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 191.6, 166.2 (d, *J* = 254 Hz), 155.9, 137.0, 134.0 (d, *J* = 10 Hz), 131.6, 131.64, 126.6, 125.3, 124.8, 120.22 (d, *J* = 40 Hz), 118.2, 115.48 (d, *J* = 21.8 Hz), 112.3, 49.3, 19.1. IR($CHCl_3$ cm^{-1}) *v*; 3436, 2924, 2852, 1665, 1428, 1230, 1155; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{14}FN_2O$ 293.1085; found: 293.1090.

***(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(4-methoxyphenyl)methanone (64)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-methoxy phenylacetylene (81.9 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 93:7) as semi solid (138 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ = 9.40 (brs, 1H), 8.28–8.24 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.34–7.29 (m, 1H), 7.17 (t, *J* = 6.9 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 2H) ,4.18 (dd, *J* = 9.4, 8.1 Hz, 2H), 3.91 (s, 3H), 3.04 (dd, *J* = 9.4, 8.1 Hz, 2H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)δ = 191.5, 164.2, 156.2, 136.9, 133.6, 128.1, 127.0 125.1, 124.9, 120.3, 119.9, 117.9, 113.7, 112.3, 55.6, 49.2, 19.1. IR($CHCl_3$ cm^{-1}) *v*; 3210, 2926, 1623, 1217, 1169; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{17}N_2O_2$ 305.1285; found: 305.1290.

(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(4-ethylphenyl)methanone (65)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-n-pentyl phenylacetylene (133 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 95:5) as semi solid (159.1 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.40 (brs, 1H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.21–4.14 (m, 2H), 3.09–2.97 (m, 2H), 2.71–2.66 (m, 2H), 1.68–1.63 (m, 2H), 1.38–1.30 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 193.0, 156.0, 149.5, 136.9, 132.9, 131.2, 128.4, 126.8, 125.1, 124.8, 120.3, 119.9, 118.0, 112.3, 49.3, 36.1, 31.4, 30.7, 22.5, 19.1, 14.0. IR($CHCl_3$ cm^{-1}) *v*; 3317, 2955, 1634, 1454, 1216; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{23}H_{25}N_2O$ 345.1961; found: 345.1939.(4-(Tert-butyl)phenyl)(4,9-dihydro-3H-pyrido[3,4-b]indol-1-yl)methanone (66)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-*tert*- butylphenylacetylene (122.6 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 95:5) as semi solid (142 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.43 (brs, 1H), 8.15 – 8.10 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.44–7.41 (m, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 4.17 (dd, *J* = 17.0, 8.2 Hz, 2H), 3.07–3.00 (m, 2H), 1.35 (s, 9H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 193.1, 157.4, 156.0, 136.9, 132.6, 131.0, 126.8, 125.4, 125.1, 124.8, 120.3, 120.0, 118.0, 112.3, 49.3, 35.2, 31.1, 19.1. IR($CHCl_3$ cm^{-1}) *v*; 3436, 2963, 1692, 1427, 1218; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{22}H_{23}N_2O$ 331.1805; found: 331.1803.

***(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(4-propylphenyl)methanone (67)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-n-propylphenylacetylene (99.2 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as semi solid (140 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.42 (brs, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.36–7.26 (m, 3H), 7.16 (t, *J* = 7.2 Hz, 1H), 4.24–4.13

(m, 2H), 3.04 (dd, *J* = 15.9, 7.0 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.70–1.65 (m, 2H), 0.97 (t, *J* = 7.0 Hz 3H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ = 193.0, 156.0, 149.3, 137.0, 133.0, 131.3, 128.5, 126.8, 125.1, 124.9, 120.3, 120.0, 118.0, 112.3, 49.3, 38.2, 24.2, 19.1, 13.8. IR($CHCl_3$ cm^{-1}) *v*; 3432, 2870, 1693, 1216; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{21}N_2O$ 317.1648; found: 317.1647.

***(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(4-ethylphenyl)methanone (68)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-ethyl phenylacetylene (89.68 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as semi solid (130.2 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$) δ = 9.42 (brs, 1H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.44–7.42 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 3H), 7.20–7.14 (m, 1H), 4.18 (dd, *J* = 9.4, 8.1 Hz, 2H), 3.07–2.99 (m, 2H), 2.76–2.71 (m, 2H), 1.29–1.25 (m, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 192.9, 156.0, 150.7, 136.9, 132.6, 131.3, 127.9, 126.8, 125.1, 124.7, 120.3, 120.0, 118.0, 112.3, 49.3, 29.1, 19.1, 15.18. IR($CHCl_3$ cm^{-1}) *v*; 3398, 2944, 1666, 1211; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{19}N_2O$ 303.1492; found: 303.1472.

***(4,9-Dihydro-3H-pyrido[3,4-b]indol-1-yl)(p-tolyl) methanone (69)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), p-tolyl acetylene (80.0 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as semi solid (131 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ = 9.45 (brs, 1H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.49–7.43 (m, 1H), 7.38–7.30 (m, 3H), 7.24–7.16 (m, 1H), 4.21 (dd, *J* = 9.4, 8.1 Hz, 2H), 3.07 (dd, *J* = 9.1, 7.8 Hz, 2H), 2.47 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 193.0, 156.0, 144.6, 136.9, 132.7, 131.2, 129.0, 126.8, 125.1, 124.8, 120.3, 120.0, 118.0, 112.3, 49.3, 21.8, 19.1. IR($CHCl_3$ cm^{-1}) *v*; 3390, 2924, 1651, 1444, 1216; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{17}N_2O$ 289.1335; found: 289.1336.

***Phenyl(9H-pyrido[3,4-b]indol-1-yl)methanone (70)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), phenylacetylene (70.3 µl, 0.62 mmol),

thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as solid (98.6 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.49 (s, 1H), 8.65 (d, *J* = 4.9 Hz, 1H), 8.38–8.33 (m, 2H), 8.22 (t, *J* = 5.6 Hz, 2H), 7.65 (t, *J* = 6.4 Hz, 3H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.42–7.36 (m, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 195.6, 141.0, 138.1, 137.7, 137.3, 132.4, 131.7, 131.2, 129.3, 128.1, 121.8, 120.7, 118.6, 112.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{13}N_2O$ 273.1022; found: 273.1024.The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[20h]

***(4-Ethylphenyl)(9H-pyrido[3,4-b]indol-1-yl)methanone (71)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-n Pentylphenylacetylene (133 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 97:3) as solid (149.6 mg, 70%), mp (197-199 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.46 (brs, 1H), 8.63 (d, *J* = 4.9 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 2H), 8.19 (t, *J* = 7.0 Hz, 2H), 7.65–7.59 (m, 2H), 7.37–7.35 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 2.74–2.69 (m, 2H), 1.72–1.67 (m, 2H), 1.42–1.34 (m, 2H), 1.28–1.20 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 195.1, 148.2, 141.0, 137.8, 137.1, 136.4, 134.7, 131.1, 129.2, 128.2, 127.5, 121.6, 120.9, 120.6, 118.2, 111.9, 36.0, 31.5, 30.8, 22.5, 14.1. IR($CHCl_3$ cm^{-1}) *v*; 3348, 2923, 1672, 1232; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{23}H_{23}N_2O$ 343.1805; found: 343.1780.

***(4-Ethylphenyl)(9H-pyrido[3,4-b]indol-1-yl)methanone (72)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 4-ethyl phenylacetylene (89.68 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as solid (123.75 mg, 66%), mp (191-193 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.46 (brs, 1H), 8.62 (d, *J* = 4.9 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 2H), 8.18 (t, *J* = 7.1 Hz, 2H), 7.64–7.61 (m, 2H), 7.40–7.36 (m, 3H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 193.0, 155.8, 150.6, 136.8, 132.9, 131.5, 131.2, 127.8, 127.6, 126.6, 125.0, 124.8, 120.4, 119.9, 117.9, 112.4, 49.1, 28.9, 19.1, 15.2. IR($CHCl_3$

cm^{-1}) *v*; 3347, 2924, 2852, 1730, 1454, 1317, 1215; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{17}N_2O$ 301.1335; found: 301.1316.

***(9H-Pyrido[3,4-b]indol-1-yl)(2-(trifluoromethyl)phenyl)methanone (73)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 2- (trifluoromethyl)phenylacetylene (87.8 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 94:6) as solid (133.8 mg, 63%), mp (193-195 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.45 (brs, 1H), 8.62 (d, *J* = 4.9 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 2H), 8.21–8.18 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.65–7.63 (m, 2H), 7.40–7.36 (m, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ = 194.6, 141.1, 140.6, 138.3, 137.4, 135.5, 133.6, 133.4 (q, *J* = 7.5 Hz), 132.0, 131.4, 129.5, 129.0, 125.0 (q, *J* = 15 Hz), 123.6 (q, *J* = 247.5 Hz), 119.1, 119.0, 112.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.0; IR($CHCl_3$ cm^{-1}) *v*; 3397, 2921, 2851, 1674, 1446, 1317, 1232, 1129; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{12}F_3N_2O$ 341.0896; found: 341.0870. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[20a]

***(9H-Pyrido[3,4-b]indol-1-yl)(2-(trifluoromethyl)phenyl)methanone (74)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 2-(trifluoromethyl) phenylacetylene (87.8 µl, 0.62 mmol), thiophenol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 96:4) as solid (129.62 mg, 61%), mp (189-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.43 (brs, 1H), 8.53 (d, *J* = 4.9 Hz, 1H), 8.21–8.16 (m, 2H), 7.83 (d, *J* = 6.9 Hz, 1H), 7.69–7.63 (m, 5H), 7.40–7.37 (m, 1H); ^{13}C NMR {1H} (125 MHz, $CDCl_3$) δ = 198.1, 141.2, 138.7, 137.8 (q, *J* = 8.8 Hz), 136.8, 135.5, 135.2, 131.8, 131.0, 129.9, 129.6, 129.2, 128.6, 128.3, 125.2 (q, *J* = 13.8 Hz), 125.0, 121.6 (q, *J* = 258.7 Hz),119.2, 112.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.0; IR ($CHCl_3$ cm^{-1}) *v*; 3385, 2924, 1654, 1494, 1317, 1214; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{12}F_3N_2O$ 341.0896; found: 341.0871.

***1-(9H-Pyrido[3,4-b]indol-1-yl)heptan-1-one (75)*:** The title compound was prepared according to the general procedure by taking tryptamine (100 mg, 0.62 mmol), 1-octyne (98.2 µl, 0.62 mmol), thiophe-

nol (6.82 µl, 0.062 mmol), TFA (47.7 µl, 0.62 mmol), $Ru(bpy)_3Cl_2$ (9.3 mg, 2 mol%) and purified by column chromatography (hexane:EA :: 99:1) as semi solid (66.5 mg, 38%). ^1H NMR (400 MHz, $CDCl_3$) δ = 10.37 (brs, 1H), 8.57 (d, *J* = 5.0 Hz, 1H), 8.18 (d, *J* = 4.5 Hz, 1H), 7.64–7.60 (m, 2H), 7.45– 7.42 (m, 1H), 7.38–7.35 (m, 1H), 3.44 (t, *J* = 6.9 Hz, 2H), 1.92–1.80 (m, 2H), 1.42–1.34 (m, 6H), 0.95–0.90 (m, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ = 204.9, 141.2, 138.1, 136.2, 131.5, 129.3, 129.2, 128.6, 121.8, 120.6, 118.9, 111.93, 37.6, 31.7, 30.9, 29.0, 24.3, 22.6. IR($CHCl_3$ cm^{-1}) *v*; 3439, 2926, 1666, 1465; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{21}N_2O$ 281.1648; found: 281.1648.

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR Spectra of all compounds and associated protocols. This material is available free of charge via the Internet at http://pubs.acs.org.

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