Synthesis, 2010, 4087-4095

Efficient Synthesis of Congeners based on a Naturally occurring Skeleton 5−7−6 Tricyclic Pyrrolo[2,1-*c*][1,4] Benzodiazepin-5-one via π-cyclization

Sudhir K. Sharma[1], *Anil K. Mandadapu*[1], *K. Kumaresan*[1],

Ashish Arora[2] *and Bijoy Kundu*[1]*

[

[1]Division of Medicinal and Process Chemistry, [2]Division of Molecular & Structural Biology, Central Drug Research Institute, CSIR, Lucknow, 226001, India.

E-mail: bijoy_kundu@yahoo.com;b_kundu@cdri.res.in Fax: +91-0522-2223405, 2223938. CDRI

Abstract :An efficient method for the synthesis of a library based on a naturally occurring 5-7-6 tricyclic benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one skeleton and its derivatives via 7-endo *trig* Pictet–Spengler π-cyclization is describe

Introduction

In recent years, libraries based on natural product inspired templates are being extensively screened for the identification of novel therapeutic candidates.[1] Accordingly, efficient syntheses of these templates for the generation of libraries have remained a challenging task for organic chemists. Out of the variety of strategies applied, C-C bond forming reactions[2] have always remained an attractive route for the synthesis of nature's repertoire of templates/pharmacophores. Recently, we applied the modified Pictet-Spengler strategy published by others[3] and us[4] and for the synthesis of libraries based on isocryptolepine[5] and phenanthridine[6] motifs derived from natural sources.

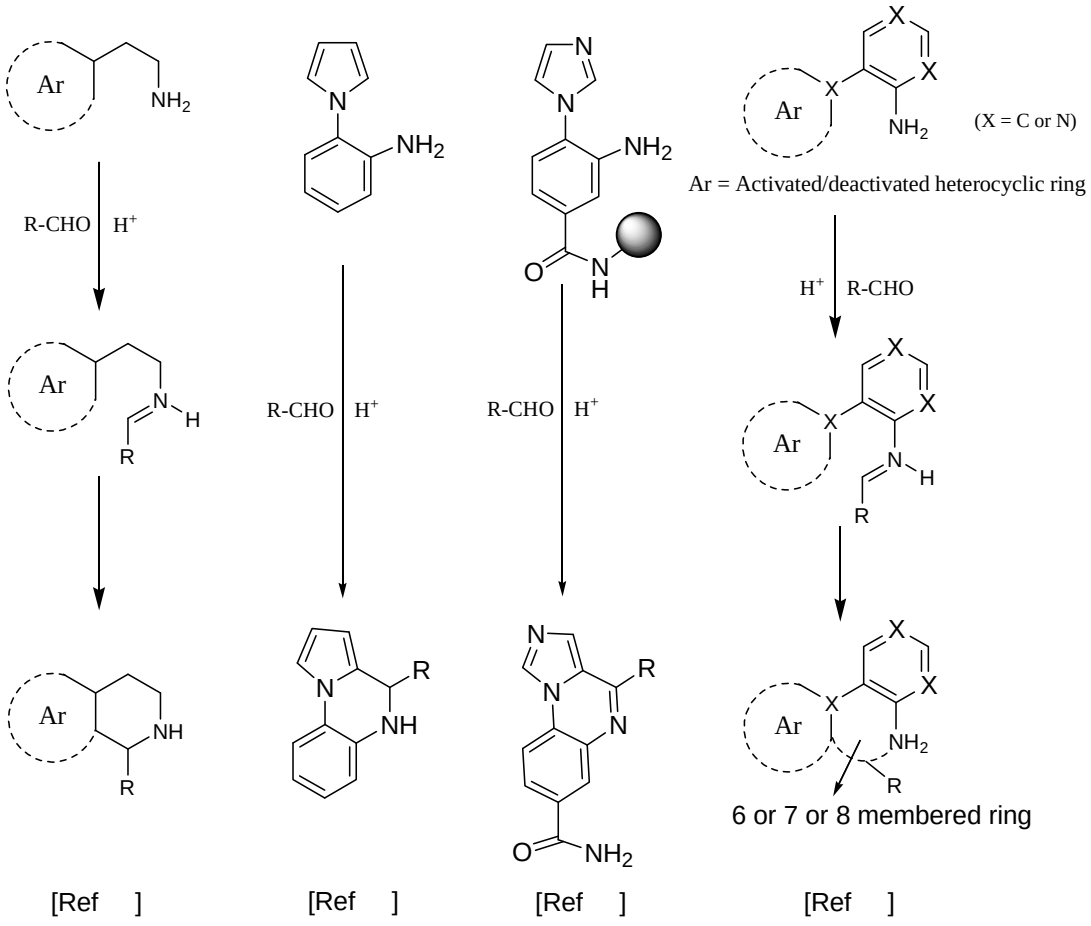


Fig 1: Chronology of the paradigm shift in the Pictet-Spengler cyclization from aliphatic amine-based substrates to arylamine-based substrates.

Although, the first aryl amine strategy for intramolecular cyclization was reported by Cheeseman *et al* in 1971 involving condensation of *N*-aryl amine pyrrole with aldehydes, their work was not discussed in the light of the principles of the Pictet-Spengler strategy reported in 1901[7] (Fig 1). In subsequent years, two reports based on the aryl amine strategy was reported involving condensation of aryl amine substrates with formaldehyde in the presence of harsh reaction condition involving neat TFA such as Bronsted acid thereby restricting its wide application. In recent years, we initiated a rationalized approach (by analyzing the electrophilic substitution pattern of heterocycles) for the wide application of

the aryl amine-based modified strategy by linking aryl amines with a host of activated (Thiazole, Pyrazole, Indole, Imidazole, Dimethoxyphenyl) and deactivated (Quinoxaline, Triazole, Tetrazole, Pyrimidine and Pyridine) heterocycles followed by their condensation with carbonyl-containing compounds under mild conditions to facilitate intramolecular cationic π-cyclizations. The motivation for our studies stemmed from the fact that the iminium ion derived from the aromatic amine will facilitate C-C bond formation more than the aliphatic amine since enhancement of the electrophilic nature of the iminium intermediate in the Pictet-Spengler reaction has been reported to be a driving force for cyclization.5 Further based on the findings by Cook et al. that amines with higher p*K*a values are relatively sluggish towards endo cyclization, we compared the p*K*a values of tryptamine 10.2 and Trp-OMe 7.29 with the aniline (in the absence of p*K*a value available for 3, aniline's p*K*a value was taken into account) 4.2, and found that for all the aryl amine substrates reported by us and others, the carbon–nitrogen double bond derived from aryl amine substrate is relatively highly electrophilic since the rate of reaction was much faster than the imines derived from Trp-OMe and tryptamine, respectively (Fig 2). Finally, a careful survey of the repertoire of substrates reported by us and others clearly suggests that an aryl or heteroaryl amine linked to either carbon or nitrogen of a heterocycle facilitates cationic cyclization under a host of Bronsted acid conditions and opens up avenues for engineering tethered biheterocycle into polyheterocyclic structures.

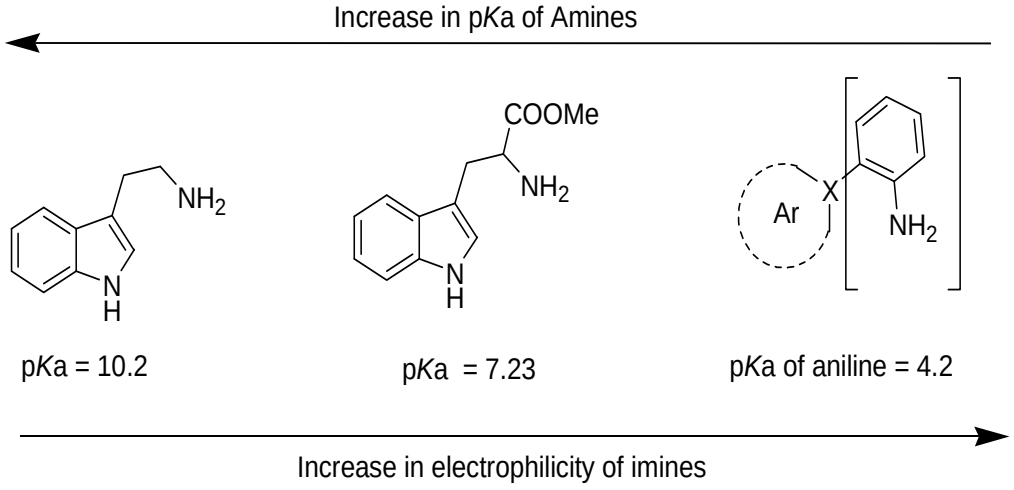


Figure 2: High order of reactivity observed in aryl amine substrates is in accordance to the findings by Cook et al. that amines with lower p*K*a values are relatively facilitate endo cyclization.

Therefore, in order to further expand the versatility of the modified strategy, we identified yet another natural product inspired template based on pyrrolo[1,4]benzodiazepinone as our target structure. We became interested in this 5-6-7 tricyclic skeleton owing to its occurrence in nature and association with antitumor activities. The pyrrolo[1,4]benzodiazepin-5-one skeleton has been found to be present in a family of naturally occurring antitumor antibiotics anthramycin[8], tomaymycin[9], prothracarcin[10] sibiromycin (**1a**)[11], tilivalline[12] and circumdatins[13], isolated from *Streptomyces*. The cytotoxic activity of these antitumor antibiotics has been attributed to their ability to bind covalently to the *C*-2 amino group of the sequence purine-guanine-purine residues within the minor groove of DNA[14] and with DNA-GC base pairs.[15]

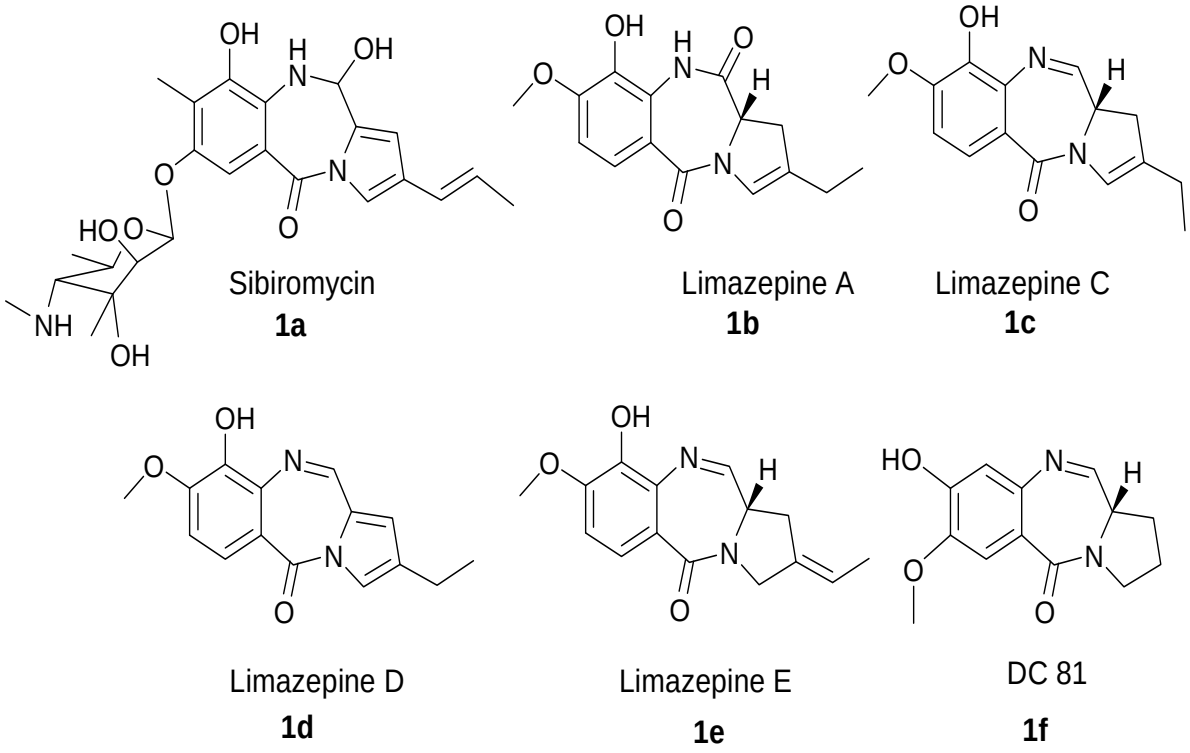


Fig. 3: Structures of antitumor antibiotics with a pyrrolo[1,4] benzodiazepine basic skeleton

They have also been reported to be associated with antibacterial, antileishmanial and herbicidal[16] activities. Recently the skeleton has been found to be present in natural products limazepine A (**1b**), limazepine B1, B2, limazepine C (**1c**), limazepine D (**1d**), limazepine E (**1e**) and limazepine F, isolated from Indonesian Micrococcus (Fig 1).[17]

Thus naturally occurring pyrrolobenzodiazepin-5-ones are 5-7-6 tricyclic molecules, and can be grouped under three chemototypes: (11a*S*)-1,11a-dihydro-5*H*-pyrrolo[2,1-*c*][1,4] benzodiazepin-5-ones containing a stereogenic centre at *C*-11a (**1b**, **1c;** Fig 1), (11a*S*)-1,2,3,11a-tetrahydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-ones containing a pyrrolidine ring (**1e**, **1f**) and 5H-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-ones and its dihydro derivative (**1a**, **1d**) having a pyrrole ring. A careful survey of the literature revealed several reports[18] dealing with the synthesis of (11a*S*)-1,11a-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-ones and 1,2,3,11a-tetrahydro-5*H*-pyrrolo[2,1-*c*][1,4]benzo diazepin-5-one, however, reports dealing with the synthesis of 5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-ones are scarce.[19]

In one of the earliest reports, indeed the latter was obtained by treating the sodium salt of pyrrole-2-carboxaldehyde with sulfonamide anhydride obtained from anthranlic acid, however, the versatility of the method was not investigated due to limited substituent diversity.[20] We proposed to apply the modified Pictet-Spengler strategy reported by us[21] with the possibility of synthesizing a diverse set of libraries based upon the recently isolated[14] naturally occurring 5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one pharmacophore. Retrosysnthetic analysis (Fig **2**) based on the modified Pictet- Spengler strategy

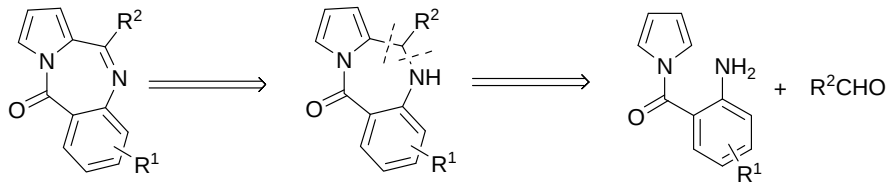
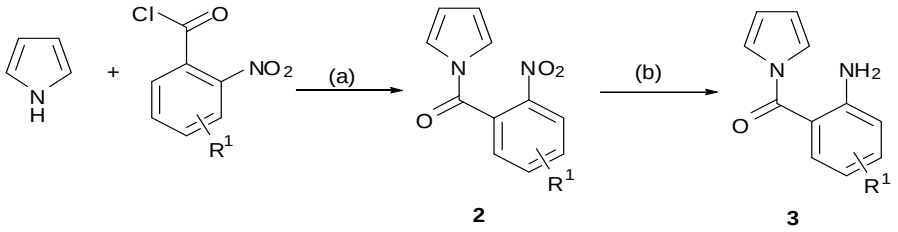


Fig. 4: Retrosynthetic analysis of 5*H*-pyrrolo[2,1-c][1,4]benzodiazepin-5-one-pharmacophore based on the modified Pictet-Spengler strategy

suggests that 5*H*-pyrrolo[2,1- c][1,4] benzo diazepin-5-one skeleton could be obtained by condensing aldehydes with the (2-amino-phenyl)-pyrrol-1-yl-methanone (pyrrole *N*-acylated aryl amine) substrates via 7- endo trig cyclization. In this communication we wish to report a straight-forward synthetic route for generating library based on a naturally occurring annulated pyrrolobenzdiazepinone skeleton using a 7-endo-trig Pictet–Spengler cyclization reaction. To the best of our knowledge this is the first report of the application of 7-endo trig cyclization leading to the generation of diazepinone rings.

Results and Discussion:

The key intermediates required for the Pictet-Spengler reaction in the form of substrates **3a-f** were obtained in two steps as depicted in Scheme **1**. The synthesis commenced with the formation of intermediates **2a-f** by treating 2-nitrobenzoylchloride derivatives with pyrrole in the presence of DMAP and Et_3N in dry DCM under nitrogen atmosphere at 0 ^{0}C.[22] The resulting nitro derivatives were then treated with Fe in HCl/ethanol under reflux to give **3a-f** in good yields. With the substrates **3a-f** in hand, their abilities to undergo a π-cyclization with structurally diverse aldehydes were investigated.

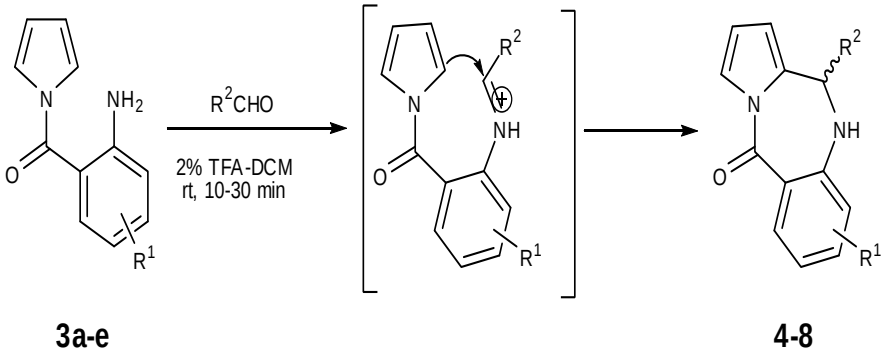


2 **3**

2a (67%), **3a** (70%); R^1 = H
2b (63%), **3b** (69%); R^1 = 5-CH_3
2c (65%), **3c** (65%); R^1 = 5-Cl
2d (66%), **3d** (63%); R^1 = 4-Cl
2e (62%), **3e** (67%); R^1 = 3-Cl
2f (38%), **3f** (60%), R^1 = 5-OCH_3

Scheme 1: General strategy for the synthesis of substrates **3a-f**; Reaction conditions: (a) DMAP, Et_3N, dry CH_2Cl_2 0^{0}C, N_2 atm, overnight (b) Fe/ HCl:C_2H_5OH (1:9), reflux ,1h

In the first instance, the substrate **3a** was subjected to the Pictet-Spengler reaction (Scheme **2**) by treating it with 4-chlorobenzaldehyde using variety of Bronsted acids. Out of the different acids (Table **1**) used, the best results were obtained when substrate **3a** was treated with 4-chlorobenzaldehyde in 2% TFA in dry DCM, at rt, which effected complete conversion of **3a** within 15 min and as expected afforded 10,11 dihydro- pyrrolo[1,2-*a*][1,4]benzo diazepin-5-one **4a** via 7-endo cyclization in 95% purity based on HPLC.



3a-e **4-8**

Scheme 2: A general strategy for the synthesis of 10,11-dihydro-5*H*-pyrrolo[2,1-c][1,4]benzodiazepin-5-ones via 7-endo cyclization

The crude product obtained after workup was purified by silica gel column chromatography using EtOAc/hexane as an eluent furnishing **4a** in 85% isolated yield. The scope and limitation of the strategy was established by treating the five substrates **3a-f** with a wide variety of structurally diverse

Table 1: Optimization of the reaction conditions for conversion of substrate **3a** to **4a.**

Entry	Reaction conditions	Temp	Time	Yield of **4a**[#]
1	1 % TFA in CH_3CN	rt	40m	30
2	1% *p*-TsOH in CH_3CN	rt	30m	20
3	1% TFA in toluene	rt	35m	45
4	2 % TFA in toluene	rt	25m	30
5	2 % TFA in CH_3CN	rt	15m	50
6	2 % TFA in CH_2Cl_2	rt	15m	85
7	EtOH	rt/heating	NR	
8	$Yb(OTf)_3$	rt	2.5h	55
9	BF_3:Et_2O	rt	1h	50

Isolated yield aryl aldehydes. For the Pictet–Spengler cyclization, 2% TFA in dry DCM at rt protocol was exclusively used and in most of the cases the cyclization was found to be complete within 10-30 min with isolated yields ranging from 56–92% (thirty five compounds) based on **4-9** (Table **2**).

Table 2: 7-endo trig cyclized products based on 10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one skeleton (**4-9**) resulting from the condensation of substrates **3a-f** and R^2CHO.

Entry	Substrate	R^2	Product	Reaction time	Yield (%)	t_R (min)[#]
1	**3a**	4-Cl-C_6H_4	**4a**	15 min	85	20.95
2	**3a**	4-NO_2-C_6H_4	**4b**	10 min	92	19.29
3	**3a**	4-Br-C_6H_4	**4c**	10 min	78	21.26
4	**3a**	4-CH_3-C_6H_4	**4d**	20 min	69	20.36
5	**3a**	4-F-C_6H_4	**4e**	15 min	76	19.63
6	**3a**	4-CN-C_6H_4	**4f**	20 min	82	18.27
7	**3a**	2,3-di-Cl-C_6H_3	**4g**	15 min	88	21.88
8	**3a**	3,4-di-Cl-C_6H_3	**4h**	15 min	78	21.86
9	**3a**	*N,N*-diMe- C_6H_4	**NR**	-	-	-
10	**3a**	2-OH-C_6H_4	**NR**	-	-	-
11	**3b**	4-NO_2-C_6H_4	**5a**	10 min	85	20.23
12	**3b**	4-Cl-C_6H_4	**5b**	15 min	81	22.16
13	**3b**	4-Br-C_6H_4	**5c**	15 min	79	22.35
14	**3b**	2,3-di-Cl-C_6H_3	**5d**	15 min	91	23.02
15	**3b**	3,4-di-Cl-C_6H_3	**5e**	15 min	89	22.95
16	**3c**	4-Cl-C_6H_4	**6a**	15 min	78	23.03
17	**3c**	4-Br-C_6H_4	**6b**	15 min	67	23.23
18	**3c**	4-NO_2-C_6H_4	**6c**	10 min	90	20.83
19	**3c**	2,3-di-Cl-C_6H_3	**6d**	10 min	91	23.93
20	**3c**	3,4-di-Cl-C_6H_3	**6e**	10 min	88	23.82
21	**3c**	4-CN-C_6H_4	**6f**	10 min	87	20.25
22	**3c**	4-F-C_6H_4	**6g**	10 min	73	21.45
23	**3c**	4- CH_3-C_6H_4	**6h**	30 min	56	22.15
24	**3d**	4-Cl-C_6H_4	**7a**	10 min	87	22.64
25	**3d**	4-Br-C_6H_4	**7b**	15 min	78	23.05
26	**3d**	4-NO_2-C_6H_4	**7c**	10 min	89	20.91
27	**3d**	4-CN-C_6H_4	**7d**	10 min	77	20.23
28	**3e**	4-Cl-C_6H_4	**8a**	15 min	71	23.13
29	**3e**	4-NO_2-C_6H_4	**8b**	10 min	82	23.27
30	**3e**	4-Br-C_6H_4	**8c**	15 min	74	23.27
31	**3e**	4-CN-C_6H_4	**8d**	10 min	79	20.81
32	**3e**	4-F-C_6H_4	**8e**	10 min	75	21.67
33	**3e**	4- CH_3-C_6H_4	**8f**	25 min	58	22.89
34	**3e**	3,4 di-Cl-C_6H_3	**8g**	10 min	80	23.98
35	**3e**	2,3 di-Cl-C_6H_3	**8h**	10 min	83	24.18
36	**3f**	4-Cl-C_6H_4	**9a**	20 min	71	
37	**3f**	4-NO_2-C_6H_4	**9b**	10 min	77	

[#]Retention time on HPLC (C18 reversed-phase column ; 150 X 4.6 mm; 5μm) with a linear gradient of 10-100% CH_3CN in water over 30 min, flow rate of 1.0 mL/min, and UV detection at 220/254. NR = No Reaction.

In general, aryl aldehydes with an electron-withdrawing group (R^2) furnished endo cyclized compounds in good yields, in contrast, aryl aldehydes with an electron-donating group either failed (Entries **9**, **10**) or furnished endo cyclized products in moderate yields (Entries **4**, **23**, **33**). Replacement of aryl aldehydes with ketones or aliphatic aldehyde failed to facilitate endo cyclization, even after extending the reaction for a longer period. This may be attributed to the following two reasons: 1) the imines resulting from aliphatic aldehydes/ketones tend to exhibit relatively poor electrophilicity than the imines derived from aromatic aldehydes and 2) The carbonyl group present between the aryl amine and the pyrrole N further contributes towards the decrease in the nucleophilicity of the aryl amine. Further, with the limited diversity used for R^1, this substitution in the aryl ring of the substrates **3** appears to have no effect on the rate of cyclization.

After successfully establishing the diazepinone ring formation via 7-endo cyclization, we next carried out oxidation of the endo cyclized products **4-8** based on 10, 11 dihydro-benzo[e]pyrrolo[1,2-*a*][1,4]diazepin-5-one with the view to generate a double bond between the *N*-10 and *C*-11 positions, an important feature present in natural compounds and considered to be essential for the aminal linkage with DNA-reactive species.

Accordingly, oxidation was carried out by treating cyclized products **4-8** with DDQ in DCM at rt (Scheme **3**). In general, conversions were found to be complete within 15 min furnishing oxidized products (**10a-k**) in excellent isolated yields (Table **3**).

Scheme 3: Generation of a double bond between the *N*-10 and *C*-11 to form 5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-ones (**10a-k**)

Table 3: 5*H*-pyrrolo[2,1-*c*][1,4]benzo diazepin-5-ones (**10**) resulting from the DDQ oxidation of **4-8**

Entry	Substrate	Product	$(M+H^+)$	Yield (%)	t_R (min)
1	**4a**	**10a**	307.3	87	24.671
2	**4c**	**10b**	351.2	88	24.571
3	**4e**	**10c**	291.2	81	22.745
4	**4g**	**10d**	341.3	84	23.019
5	**5a**	**10e**	332.2	87	23.169
6	**5b**	**10f**	321.1	83	22.120
7	**6c**	**10g**	352.2	79	18.096
8	**7c**	**10h**	352.3	92	19.376
9	**8b**	**10i**	352.1	76	23.430
10	**8d**	**10j**	332.3	92	19.376
11	**8g**	**10k**	375.1	76	23.430

Conclusions

In conclusion we have developed a fast, efficient and versatile method for the synthesis of a recently isolated naturally occurring 5-7-6 tricyclic skeleton pyrrolo[1,2-*a*][1,4]benzodiazepin-5-one and its derivatives via the formation of diazepinone ring using 7-endo cyclization strategy. The pyrrole *N*-acylated aryl amine substrate used in the present investigation is a new addition to the repertoire of "second generation substrates" for the modified Pictet-Spengler reaction reported earlier by us. Currently work is in progress to extend the methodology for the synthesis of other biologically active compounds having diazepinone rings.

Experimental Section

All solvents were commercially available and used without purification. All products were characterized by ^{1}H NMR, ^{13}C NMR, ESMS, IR and HPLC. Analytical TLC was performed using 2.5 x 5 cm plated coated with a 0.25 mm thickness of silica gel. 60F-254 Merck and visualization was accomplished with UV light and iodine. Column chromatography was performed using silica gel 60 Thomas Baker (100-200 mesh). ^{1}H NMR spectra (200/300/600 MHz) are reported as follows: chemical shifts in ppm downfield from TMS as internal standard (δ scale), multiplicity [br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, o=overlapped, integration and coupling constant (Hz)]. All ^{13}C NMR spectra (50/75/150 MHz) were recorded at 25 ^{0}C with complete proton decoupling and reported in ppm. Elemental analyses were performed on a Carlo Erba 1108 microanalyzer or Elementar's Vario EL III microanalyzer in the SAIF division of our institute. Analytical HPLC were performed on C-18 reverse-phase column (150 mm x 4.8 mm). Mass spectra were recorded on a Merck MS-8000 spectrometer and HR/EI Mass spectra were done on JEOL-600H at 70eV. Melting points reported were uncorrected.

General procedure for the preparation of substrates 2a-f:

To a solution of pyrrole (10 mmol), Et_3N (7.4 mmol), and DMAP (0.74 mmol) in dry CH_2Cl_2, under nitrogen atmosphere, the derivatives of 2-nitrobenzoylchlorides (prepared by refluxing 2-nitrobenzoic acid derivatives with thionyl chloride) were added slowly and the solution was left stirring for overnight. The reaction mixture was then evaporated, dissolve in ethylacetate washed with $KHSO_4$, $NaHCO_3$ solutions and then organic layer was separated in DCM and dried over anhydrous Na_2SO_4. The compounds were purified by column chromatography using ethylacetate:hexane (1:10) as eluent.

(2-nitrophenyl)(1*H*-pyrrol-1-yl)methanone (2a):
Yield = 2.16 g (67%), yellow solid, mp 74-76^{o}C, R_f = 0.35 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3335, 1699, 1530, 1334, 1066 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.30 (1H, dd, *J* = 8.1, 1.2 Hz, ArH), 7.82 (1H, td, *J* = 7.4, 1.3 Hz, ArH), 7.77 (1H, td, *J* = 7.8, 1.6 Hz, ArH), 7.61-7.58 (1H, m, ArH), 7.06 (2H, brs, ArH), 6.33 (2H, s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.4, 145.9, 134.5, 131.6, 130.3, 129.0, 124.8, 120.1, 114.2 ppm; mass (ES^+) *m/z* 217.1 (M^+ + 1); Anal. Calcd for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.73; N, 12.96; Found: C, 61.14; H, 3.71; N, 12.95.

(5-methyl-2-nitrophenyl)(1*H*-pyrrol-1-yl)methanone (2b):
Yield = 2.16 g (63%), light yellow solid, mp 101-103^{o}C, R_f = 0.30 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3416, 3047, 1714, 1337, 1174 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (1H, d, *J* = 8.4 Hz, ArH), 7.82 (1H, td, *J* = 8.7, 1.3 Hz, ArH), 7.37 (1H, t, *J* = 0.6, Hz, ArH),7.02 (2H, brs, ArH) 6.32 (2H, s, ArH), 2.52 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 164.7, 146.3, 143.7, 131.9, 130.5, 129.5, 124.9, 120.1, 114.1, 21.6 ppm; mass (ES^+) *m/z* 231.1 (M^+ + 1); Anal. Calcd for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17; Found: C, 62.62; H, 4.37; N, 12.16.

(5-Chloro-2-nitro-phenyl)-pyrrol-1-yl-methanone (2c):
Yield = 2.42 g (65%), yellow solid, mp 130-131^{o}C, R_f = 0.34 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3434, 3046, 1704, 1412, 1338, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.25 (1H, d, *J* = 8.8 Hz, ArH), 7.68 (1H, dd, *J* = 8.8, 2.2 Hz, ArH), 7.57 (1H, d, *J* = 2.1, Hz, ArH), 7.08 (2H, brs, ArH), 6.35 (2H, s, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 162.9, 144.2, 141.5, 132.0, 131.6, 129.2, 126.4, 120.1, 114.7 ppm; mass (ES^+) *m/z* 251.2 (M^+ + 1); Anal. Calcd for $C_{11}H_7ClN_2O_3$: C, 52.71; H, 2.82; N, 11.18; Found: C, 52.75; H, 2.80; N, 11.15.

(4-chloro-2-nitrophenyl)(1*H*-pyrrol-1-yl)methanone (2d):
Yield = 2.46 g (66%), yellow solid, mp 92-93^{o}C, R_f = 0.40 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3406, 1704, 1540, 1474 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.28 (1H, d, *J* = 2.0 Hz, ArH), 7.79 (1H, dd, *J* = 8.2, 2.0 Hz, ArH), 7.55 (1H, d, *J* = 8.2, Hz, ArH), 7.08 (2H, brs, ArH), 6.34 (2H, s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.5, 146.7, 137.8, 134.5, 130.3, 128.8, 125.3, 120.1, 114.6, ppm; mass (ES^+) *m/z* 251.1 (M^+ + 1); Anal. Calcd for $C_{11}H_7ClN_2O_3$: C, 52.71; H, 2.82; N, 11.18; Found: C, 52.73; H, 2.80; N, 11.16.

(3-chloro-2-nitrophenyl)(1*H*-pyrrol-1-yl)methanone(2e):
Yield = 2.31 g (62%), yellow solid, mp 106-107^{o}C, R_f = 0.32 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3141, 1702, 1539, 1466, 1342 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.74 (1H, d, *J* = 7.8 Hz, ArH), 7.64-7.50 (2H, m, ArH), 7.15 (2H, s, ArH), 6.38 (2H, s, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.6, 133.9, 131.7, 130.2, 127.7, 127.6, 120.7, 114.7 ppm; mass (ES^+) *m/z* 251.1 (M^+ + 1); Anal. Calcd for $C_{11}H_7ClN_2O_3$: C, 52.71; H, 2.82; N, 11.18; Found: C, 52.74; H, 2.81; N, 11.16.

(5-methoxy-2-nitrophenyl)(1*H*-pyrrol-1-yl)methanone (2f):
Yield = 1.40 g (38%), yellow liquid, R_f = 0.40 (2:8 EtOAc:Hexane), IR (Neat) ν_{max} 3022, 2926, 2360, 1712, 1586, 1521, 1486, 1340 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.33 (1H, d, *J* = 9.2 Hz, ArH), 7.40-7.14 (4H, m, ArH), 6.36 (2H, s, ArH), 3.94 (3H, s, OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 164.2, 163.9, 137.9, 132.2, 127.6, 116.6, 114.3, 113.9, 56.8 ppm; mass (ES^+) *m/z* 247.2 (M^+ + 1); Anal. Calcd for $C_{12}H_{10}N_2O_4$: C, 58.54; H, 4.09; N, 11.38;; Found: C, 58.56; H, 4.079; N, 11.41.

General procedure for the preparation of substrates 3a-f:
A solution of the **2a-f** (0.23 g, 0.88 mmol) in HCl:EtOH (1:5) and Fe (0.16 g, 2.8 mmol) was refluxed under nitrogen atmosphere for 1h. After completion of reduction, the reaction mixture was allowed to cool down and then evaporated in vacuo, the pH of the solution is made slightly basic (pH 8) by the addition of solid $NaHCO_3$.The remaining iron trace was removed magnetically by the help of magnetic rode and then ethyl acetate (50 mL) was added to the mixture and filtered through a bed of celite^{R}. The organic layer was finally washed with water (50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated to dryness under reduced pressure. The crude product was purified on a silica gel column using ethyl acetate: hexane (1:5, v/v) as eluent to afforded **3a-f**.

(2-aminophenyl)(1*H*-pyrrol-1-yl)methanone (3a):
Yield = 1.20 g (70%), brown solid, mp 62-64^{o}C, R_f = 0.48 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3481, 3379, 1673, 1616 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (1H, dd, *J* = 7.9, 1.4 Hz, ArH), 7.33-7.25 (3H, m, ArH), 6.77-6.69 (2H, m, ArH), 6.33 (2H, t, *J* = 2.3 Hz, ArH), 5.15 (2H, brs, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.3, 149.7, 133.6, 131.6, 121.4, 116.9, 116.2, 114.3, 112.6 ppm; mass (ES^+) *m/z* 187.0 (M^+ + 1); Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04; Found: C, 70.91; H, 5.43; N, 15.06.

(2-amino-5-methylphenyl)(1*H*-pyrrol-1-yl)methanone (3b):
Yield = 1.20 g (69%), white solid, mp 66-68^{o}C, R_f = 0.66 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3480, 3381, 1675, 1597, 1337 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.27 (2H, t, *J* = 2.4 Hz, ArH), 7.23-7.22 (1H, m, ArH), 7.13 (1H, dd, *J* = 8.3, 1.7 Hz, ArH), 6.68 (1H, d, *J* = 8.3 Hz, ArH), 6.33 (2H, t, *J* = 2.3 Hz, ArH), 4.96 (2H, brs, NH_2), 2.24 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 168.4, 147.4, 134.6, 131.3, 125.6, 121.5, 117.1, 114.6, 112.6, 20.3 ppm; mass (ES^+) *m/z* 200.9 (M^+ + 1); Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99; Found: C, 71.96; H, 6.07; N, 13.98.

(2-amino-5-chlorophenyl)(1*H*-pyrrol-1-yl)methanone (3c):
Yield = 1.14 g (65%), brown solid, mp 108-110^{o}C, R_f = 0.54 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3476, 3375, 1670, 1620, 1477, 1346 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41 (1H, d, *J* = 2.5 Hz, ArH), 7.27-7.23 (3H, m, ArH), 7.70 (1H, d, *J* = 8.7 Hz, ArH), 6.35 (2H, t, *J* = 2.3 Hz, ArH), 5.14 (2H, brs, NH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 167.2, 148.2, 133.7, 130.7, 121.5, 121.1, 118.4, 115.5, 113.3 ppm; mass (ES^+) *m/z* 221.0 (M^+ + 1); Anal. Calcd for $C_{11}H_9ClN_2O$: C, 59.88; H, 4.11; N, 12.70; Found: C, 59.85; H, 4.13; N, 12.71.

(2-amino-4-chlorophenyl)(1*H*-pyrrol-1-yl)methanone (3d):
Yield = 1.10 g (63%), white solid, mp 111-113^{o}C, R_f = 0.72 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3453, 3352, 1668, 1618, 1470, 1334 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39 (1H, d, *J* = 8.5 Hz, ArH), 7.28-7.25 (2H, m, ArH), 6.79 (1H, d, *J* = 2.0 Hz, ArH), 6.70 (1H, dd, *J* = 8.5, 2.0 Hz, ArH), 6.36 (2H, t, *J* = 2.3 Hz, ArH), 5.32 (2H, brs, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.7, 150.8, 139.9, 133.1, 121.5, 116.7, 116.5, 113.0, 112.8 ppm; mass (ES^+) *m/z* 221.0 (M^+ + 1); Anal. Calcd for $C_{11}H_9ClN_2O$: C, 59.88; H, 4.11; N, 12.70; Found: C, 59.91; H, 4.10; N, 12.67.

(2-amino-3-chlorophenyl)(1*H*-pyrrol-1-yl)methanone (3e):
Yield = 1.18 g (67%), white solid, mp 117-119^{o}C, R_f = 0.36 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3485, 3383, 1676, 1614, 1466, 1334 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46-7.34 (2H, m, ArH), 7.25 (2H, s, ArH), 6.67 (1H, t, *J* = 7.9 Hz, ArH), 6.34 (2H, s, ArH), 5.60 (2H, brs, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.8, 145.9, 133.4, 130.3, 121.5, 120.7, 116.0, 115.6, 113.1 ppm; mass (ES^+) *m/z* 221.0 (M^+ + 1); Anal. Calcd for $C_{11}H_9ClN_2O$: C, 59.88; H, 4.11; N, 12.70; Found: C, 59.85; H, 4.12; N, 12.72.

(2-amino-5-methoxyphenyl)(1*H*-pyrrol-1-yl)methanone (3f):
Yield = 0.527 g (60%), yellow solid, mp 49-51^{o}C, R_f = 0.46 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3685, 3382, 3021, 2361, 1685, 1520, 1430, 1327 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.27 (2H, d, *J* = 1.3 Hz, ArH), 7.02-6.99 (1H, m, ArH), 6.84-6.81 (2H, m, ArH), 6.34 (2H, t, *J* = 1.5 Hz, ArH), 5.63 (2H, brs, NH_2), 3.65 (3H, s, OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 167.2, 149.0, 144.5, 121.8, 121.1, 118.2, 113.7, 113.3, 112.6, 55.4 ppm; mass (ES^+) *m/z* 217.0 (M^+ + 1); Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96; Found: C, 66.67; H, 5.58; N, 12.93.

General procedure for the Pictet-Spengler reaction:

A mixture of substrate **3a-f** (0.150g) and corresponding aldehydes (1.1eq) were treated with 2 % solution of trifluoroacetic acid in dry DCM (5 mL). The reaction mixture was allowed to stir at rt for given time (Table 2). After completion of reaction, the reaction mixture was washed with aq. $NaHCO_3$ (20 mL) and extracted with DCM (2x30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified on a silica gel column using ethyl acetate/hexane (1:5, v/v) as eluent to afford **4a-h, 5a-e, 6a-h, 7a-d, 8a-h, 9a-b**.

11-(4-chlorophenyl)-10,11-dihydro-5H-pyrrolo[2,1-c][1,4]benzodiazepin-5-one (4a):
Yield = 0.211g (85%), yellow solid, mp 150-152^{o}C, R_f = 0.48 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3325, 1715, 1630, 1482, 1432, 1328, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.39 (1H, dd, *J* = 8.3, 1.4 Hz, ArH), 7.70-7.68 (1H, m, ArH), 7.41-7.34 (5H, m, ArH), 7.77 (1H, td, *J* = 7.2, 0.9 Hz, ArH), 6.74 (1H, d, *J* = 8.1 Hz, ArH), 6.19 (1H, t, *J* = 3.3 Hz, ArH), 5.48 (1H, t, *J* = 1.0 Hz, ArH), 5.35 (1H, s, ArH), 4.71 (1H, brs, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.8, 149.2, 137.7, 134.8, 134.6, 134.2, 129.4, 129.2, 122.8, 120.3, 119.6, 116.4, 111.6, 111.4, 58.5 ppm; mass (ES^+) *m/z* 309.1 (M^+ + 1); Anal. Calcd for $C_{18}H_{13}ClN_2O$: C, 70.02; H, 4.24; N, 9.07; Found: C, 70.05; H, 4.25; N, 9.09.

11-(4-nitrophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (4b):
Yield = 0.237 g (92%), yellow solid, mp 170-172^{o}C, R_f = 0.32 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3309, 1714, 1630, 1485, 1434, 1328 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.37 (1H, d, *J* = 1.4 Hz, ArH), 8.22 (2H, dd, *J* = 7.1, 1.8 Hz, ArH), 7.72-7.70 (1H, m, ArH), 7.53 (2H, d, *J* = 8.5 Hz, ArH), 7.42-7.36 (1H, m, ArH), 6.98 (1H, td, *J* = 7.2, 1.0 Hz, ArH), 6.81-6.78 (1H, m, ArH), 6.23 (1H, t, *J* = 3.3 Hz, ArH), 5.59-5.54 (2H, m, ArH), 4.89 (1H, brs, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.5, 148.5, 146.8, 134.7, 134.3, 131.9, 128.6, 123.6, 122.3, 119.7, 119.6, 115.8, 111.4, 111.2, 56.7 ppm; mass (ES^+) *m/z* 320.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{13}N_3O_3$: C, 67.71; H, 4.10; N, 13.16; Found: C, 67.72; H, 4.11; N, 13.14.

11-(4-bromophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (4c):
Yield = 0.221 g (78%), yellow solid, mp 145-147^{o}C, R_f = 0.62 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3326, 1725, 1632, 1482, 1432, 1327 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (1H, dd, *J* = 8.3, 1.5 Hz, ArH), 7.70-7.68 (1H, m, ArH), 7.57-7.52 (2H, m, ArH), 7.39-7.28 (3H, m, ArH), 7.00-6.95 (1H, m, ArH), 6.75-6.73 (1H, m, ArH), 6.98 (1H, t, *J* = 3.3 Hz, ArH), 5.49-5.47 (1H, m, ArH), 5.33 (1H, s, CH), 4.72 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.8, 149.2, 138.2, 134.8, 134.0, 132.2, 129.8, 122.8, 120.4, 119.6, 116.4, 111.6, 111.4, 58.6 ppm; mass (ES^+) *m/z* 353.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{13}BrN_2O$: C, 61.21; H, 3.71; N, 7.93; Found: C, 61.24; H, 3.70; N, 7.91.

11-(4-methylphenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (4d):
Yield = 0.160 g (69%), brown solid, mp 82-83^{o}C, R_f = 0.31 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3345, 2924, 1725, 1659, 1605, 1481, 1432, 1325, 1164 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 (1H, d, *J* = 8.1 Hz, ArH), 7.70 (1H, d, *J* = 1.1 Hz , ArH), 7.40-7.24 (5H, m, ArH), 6.98 (1H, t, *J* = 7.6 Hz, ArH), 6.74 (1H, d, *J* = 8.3 Hz, ArH), 6.19 (1H, t, *J* = 3.0 Hz, ArH), 5.46 (1H, s, ArH), 5.32 (1H, s, ArH), 4.72 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 164.0, 149.8, 138.7, 136.2, 135.1, 134.8, 134.6, 129.7, 128.0, 122.5, 120.0, 119.4, 116.3, 111.5, 111.2, 59.0, 21.3 ppm; mass (ES^+) *m/z* 289.1 (M^+ + 1); Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72; Found: C, 79.16; H, 5.56; N, 9.73.

11-(4-fluorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (4e):
Yield = 0.191g (76%), white solid, mp 139-140^{o}C, R_f = 0.46 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3337, 1625, 1488, 1432, 1322 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.03-7.99 (1H, m, ArH), 7.74 (1H, d, *J* = 4.5 Hz, ArH), 7.52-7.50 (1H, m, ArH), 7.39-7.30 (1H, m, ArH), 7.14-7.03 (5H, m, ArH), 6.80-6.71 (1H, m, ArH), 6.29 (1H, t, *J* = 3.2 Hz, ArH), 5.94-5.91 (1H, m, ArH), 5.68 (1H, d, *J* = 4.5 Hz, NH); ^{13}C NMR (50 MHz, DMSO-d_6) δ = 163.6, 159.0, 135.9, 134.7, 133.3, 133.2, 129.5, 129.3, 121.4, 119.9, 118.1, 115.3, 114.9, 114.1, 111.6, 110.5, 54.5 ppm; mass (ES^+) *m/z* 293.1 (M^+ + 1); Anal. Calcd for $C_{18}H_{13}FN_2O$: C, 73.96; H, 4.48; N, 9.58; Found: C, 73.94; H, 4.49; N, 9.59.

4-(5-oxo-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-11-yl)benzonitrile (4f):
Yield = 0.203g (82%), brown solid, mp 226-227^{o}C, R_f = 0.41 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3353, 1649, 1482, 1322, 1160 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.0 (1H, dd, *J* = 8.3, 1.4 Hz ArH), 7.94 (1H, d, *J* = 5.3 Hz, ArH), 7.77 (2H, d, *J* = 8.3 Hz, ArH), 7.57-7.55 (1H, m, ArH), 7.41-7.36 (1H, m, ArH), 7.24 (1H, d, *J* = 8.2 Hz, ArH), 7.07 (1H, d, *J* = 7.7 Hz, ArH), 6.80-6.74 (1H, m, ArH), 6.35 (1H, t, *J* = 3.2 Hz, ArH), 6.11-6.09 (1H, m, ArH), 5.88 (1H, d, *J* = 5.2 Hz, NH); ^{13}C NMR (50 MHz, DMSO-d_6) δ = 163.4, 149.1, 145.7, 134.9, 133.3, 132.3, 131.8, 128.2, 121.6, 119.9, 118.5, 118.4, 114.1, 111.7, 111.1, 110.3, 54.5 ppm; mass (ES^{+}) *m/z* 300.2 (M^{+} + 1); Anal. Calcd for $C_{19}H_{13}N_3O$: C, 76.24; H, 4.38; N, 14.04; Found: C, 76.21; H, 4.39; N, 14.06.

11-(2,3-dichlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (4g):
Yield = 0.218g (88%), yellow solid, mp 160-161^{o}C, R_f = 0.48 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3325, 1626, 1427, 1326, 1115 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.15 (1H, dd, *J* = 8.3, 1.5 Hz, ArH), 7.59-7.54 (2H, m, ArH), 7.39-7.20 (4H, m, ArH), 7.07 (1H, d, *J* = 8.3 Hz, ArH), 6.87-6.80 (1H, m, ArH), 6.22 (1H, t, *J* = 3.3 Hz, ArH), 5.85 (1H, d, *J* = 2.8 Hz, ArH), 5.60-5.58 (1H, m, NH); ^{13}C NMR (50 MHz, $CDCl_3$+ DMSO-d_6) δ = 163.2, 149.5, 138.8, 134.4, 133.3, 132.6, 132.3, 130.1, 128.5, 127.8, 121.7, 119.9, 118.9, 114.8, 111.5, 110.2, 54.6 ppm; mass (ES^{+}) *m/z* 343.2 (M^{+} + 1); Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16; Found: C, 62.99; H, 3.52; N, 8.16.

11-(3,4-dichlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (4h):
Yield = 0.198g (78%), yellow solid, mp 140-141^{o}C, R_f = 0.50 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3313, 1628, 1322, 1131 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.03 (1H, d, *J* = 8.2 Hz, ArH), 7.82 (1H, d, *J* = 7.8 Hz, ArH), 7.57 (2H, d, *J* = 8.0 Hz, ArH) 7.43-7.30 (2H, m, ArH), 7.04 (2H, t, *J* = 8.0 Hz, ArH), 6.79 (2H, t, *J* = 7.2 Hz, ArH), 6.34 (1H, s, ArH), 6.06 (1H, s, ArH), 5.78 (1H, d, *J* = 4.6 Hz, NH); ^{13}C NMR (50 MHz, DMSO-d_6) δ = 163.4, 149.1, 141.1, 134.9, 133.4, 132.0, 131.1, 130.6, 130.2, 129.3, 127.7, 121.7, 119.9, 118.5, 114.2, 111.7, 111.0, 54.0 ppm; mass (ES^{+}) *m/z* 343.2 (M^{+} + 1); Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16; Found: C, 62.97; H, 3.53; N, 8.17.

7-methyl-11-(4-nitrophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (5a):
Yield = 0.212 g (85%), yellow solid, mp 186-188^{o}C, R_f = 0.38 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3308, 1724, 1631, 1507, 1409, 1330 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.23-8.20 (2H, m, ArH), 8.14 (1H, s, ArH), 7.73-7.71 (1H, m, ArH), 7.53-7.50 (2H, m, ArH), 7.27-7.19 (1H, m, ArH), 6.73-6.68 (1H, m, ArH), 6.22 (1H, t, *J* = 3.3 Hz, ArH), 5.58 (1H, d, *J* = 1.9 Hz, ArH), 5.51 (1H, s, ArH), 4.76 (1H, brs, NH), 2.31 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.7, 147.9, 146.6, 146.3, 136.3, 134.4, 132.8, 130.2, 128.9, 124.1, 123.0, 119.8, 116.7, 111.7, 111.6, 58.3, 20.4 ppm; mass (ES^{+}) *m/z* 334.2 (M^{+} + 1); Anal. Calcd for $C_{19}H_{15}N_3O_3$: C, 68.46; H, 4.54; N, 12.61; Found: C, 68.43; H, 4.56; N, 12.62.

11-(4-chlorophenyl)-7-methyl-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (5b):
Yield = 0.196 g (81%), yellow solid, mp 168-170^{o}C, R_f = 0.66 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3332, 2930, 1629, 1491, 1316 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.17 (1H, s, ArH), 7.70-7.68 (1H, m, ArH), 7.39-7.32 (4H, m, ArH), 7.20-7.16 (1H, m, ArH), 6.65 (1H, d, *J* = 8.2 Hz, ArH), 6.18 (1H, t, *J* = 3.3 Hz, ArH), 5.46 (1H, s, ArH), 5.30 (1H, s, CH), 5.58 (1H, brs, NH), 2.31 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$); δ = 163.9, 147.2, 137.9, 136.1, 134.7, 134.4, 129.9, 129.5, 129.3, 122.8, 121.6, 119.7, 116.6, 112.7, 111.5, 111.4, 107.0, 58.9, 20.5 ppm; mass (ES^{+}) *m/z* 323.2 (M^{+} + 1); Anal. Calcd for $C_{19}H_{15}ClN_2O$: C, 70.70; H, 4.68; N, 8.68; Found: C, 70.74; H, 4.66; N, 8.66.

11-(4-bromophenyl)-7-methyl-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (5c):
Yield = 0.217 g (79%), yellow solid, mp 153-155^{o}C, R_f = 0.42 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3329, 1722, 1635, 1497, 1405, 1317, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (1H, s, ArH), 7.70-7.69 (1H, m, ArH), 7.55-7.52 (2H, m,ArH), 7.29 (2H, d, *J* = 8.4 Hz ArH), 7.19 (1H, dd, *J* = 8.2, 2.0 Hz, ArH), 6.65 (1H, d, *J* = 8.2 Hz, ArH), 6.18 (1H, t, *J* = 3.3 Hz, ArH), 5.47 (1H, d, *J* = 1.1 Hz, ArH), 5.29 (1H, s, ArH), 4.57 (1H, s, NH), 2.31 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.9, 147.1, 138.4, 136.1, 134.3, 134.2, 132.2, 129.8, 127.7, 122.8, 122.7,119.7, 116.4, 111.5, 111.4, 58.8, 20.5 ppm; mass (ES^+) *m/z* 367.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{15}BrN_2O$: C, 62.14; H, 4.12; Br, 21.76; N, 7.63; Found: C, 62.17; H, 4.10; N, 7.63.

11-(2,3-dichlorophenyl)-7-methyl-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (5d):
Yield = 0.243 g (91%), yellow solid, mp 159-161^{o}C, R_f = 0.58 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3319, 1632, 1505, 1411, 1319 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.10 (1H, s, ArH), 7.80-7.78 (1H, m, ArH), 7.38 (1H, dd, *J* = 7.9, 1.6 Hz, ArH), 7.19-7.09 (2H, m, ArH), 7.03 (1H, dd, *J* = 7.8, 1.4 Hz, ArH), 6.60 (1H, d, *J* = 8.2 Hz, ArH), 6.26 (1H, t, *J* = 3.3 Hz, ArH), 5.90 (1H, d, *J* = 3.4 Hz, ArH), 5.76 (1H, t, *J* = 2.2 Hz, ArH), 4.57 (1H, d, *J* = 3.4 Hz, NH), 2.27 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.9, 145.8, 139.8, 136.2, 134.2, 133.8, 132.1, 131.1, 130.4, 130.3, 127.9, 127.6, 122.9, 120.0, 117.6, 111.8, 111.5, 56.2, 20.5 ppm; mass (ES^+) *m/z* 357.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{14}Cl_2N_2O$: C, 63.88; H, 3.95; N, 7.84; Found: C, 63.84; H, 3.97; N, 7.86.

11-(3,4-dichlorophenyl)-7-methyl-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (5e):
Yield = 0.238 g (89%), yellow solid, mp 157-158^{o}C, R_f = 0.38 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3314, 1629, 1500, 1407, 1318, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (1H, s, ArH), 7.70-7.69 (1H, m, ArH), 7.49-7.44 (2H, m, ArH), 7.23-7.19 (2H, m, ArH), 6.68 (1H, d, *J* = 8.2Hz, ArH), 6.20 (1H, t, *J* = 3.2 Hz, ArH), 5.53 (1H, s, ArH), 5.30 (1H, s, ArH), 4.64 (1H, brs, NH), 2.31 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.8, 146.7, 139.6, 136.2, 134.3, 133.5, 133.2, 133.8, 132.8, 130.9, 130.0, 127.4, 122.9, 119.8, 116.5, 111.6, 58.2, 20.5 ppm; mass (ES^+) *m/z* 357.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{14}Cl_2N_2O$: C, 63.88; H, 3.95; N, 7.84; Found: C, 63.70; H, 3.92;N, 7.81.

7-chloro-11-(4-chlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6a):
Yield = 0.182 g (78%), yellow solid, mp 150-152^{o}C, R_f = 0.38 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3312, 1628, 1605, 1479, 1409, 1312, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (1H, d, *J* = 2.4 Hz, ArH), 7.67-7.65 (1H, m, ArH), 7.40-7.28 (5H, m, ArH), 6.70 (1H, d, *J* = 8.7 Hz, ArH), 6.20 (1H, t, *J* = 3.2 Hz, ArH), 5.51 (1H, s, ArH), 5.34 (1H, s, ArH), 4.77 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 167.2, 148.2, 147.6, 137.3, 134.8, 133.7, 130.7, 129.4, 129.3, 125.5, 122.9, 121.5, 121.1, 118.4, 115.5, 113.3, 111.9, 58.4 ppm; mass (ES^+) *m/z* 343.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16; Found: C, 62.97; H, 3.52; N, 8.16.

11-(4-bromophenyl)-7-chloro-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6b):
Yield = 0.176 g (67%), yellow solid, mp 166-167^{o}C, R_f = 0.38 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3313, 1627, 1481, 1407, 1310, 1164 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.35 (1H, d, *J* = 2.5 Hz, ArH), 7.67-7.65 (1H, m, ArH), 7.54 (2H, dd, *J* =6.6, 1.8 Hz, ArH), 7.32-7.28 (3H, m, ArH), 6.70 (1H, d, *J* = 8.7 Hz, ArH), 6.20 (1H, t, *J* = 3.3 Hz, ArH), 5.51 (1H, t, *J* = 2.0 Hz, ArH), 5.33 (1H, s, ArH), 4.77 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 162.7, 147.6, 137.8, 134.8, 133.7, 133.6, 132.3, 129.7, 125.4, 122.9, 122.8, 121.1, 117.3, 111.9, 111.8, 58.4 ppm; mass (ES^+) *m/z* 387.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}BrClN_2O$: C, 55.77; H, 3.12; N, 7.23; Found: C, 55.78; H, 3.10; N, 7.25.

7-chloro-11-(4-nitrophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6c):
Yield = 0.216 g (90%), yellow solid, mp 208-210°C, R_f = 0.45 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3306, 1630, 1488, 1409, 1318, 1121 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 8.32 (1H, s, ArH), 8.24 (2H, d, , *J* = 8.3 Hz, ArH), 7.69 (1H, s, ArH), 7.56 (2H, d, *J* = 8.3 Hz, ArH), 7.33 (1H, d, *J* = 8.5 Hz, ArH), 6.76 (1H, d, *J* = 8.8 Hz, ArH), 6.25 (1H, s, ArH), 5.61 (1H, s, ArH), 5.55 (1H, s, CH), 4.94 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$+DMSO-d_6) δ = 161.9, 146.9, 146.6, 146.4, 133.9, 132.1, 130.8, 128.0, 122.9, 122.8, 121.7, 121.4, 115.4, 111.2, 110.9, 55.1 ppm; mass (ES^+) *m/z* 354.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}ClN_3O_3$: C, 61.11; H, 3.42; N, 11.88; Found: C, 61.15; H, 3.40; N, 11.87.

7-chloro-11-(2,3-dichlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6d):
Yield = 0.233 g (91%), yellow solid, mp 186-188°C, R_f = 0.62 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3363, 1636, 1481, 1413, 1307 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 8.28 (1H, s, ArH), 7.77 (1H, d, *J* = 1.4 Hz, ArH), 7.40 (1H, d, *J* = 7.3 Hz, ArH), 7.22 (1H, s, ArH), 7.13 (1H, t, *J* = 7.9 Hz, ArH), 7.00 (1H, d, *J* = 8.6 Hz, ArH), 6.66 (1H, d, *J* = 8.6 Hz, ArH) 6.28 (1H, s, ArH), 5.93 (1H, s, ArH), 5.80 (1H, s, CH), 5.18 (1H, brs, NH); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ = 162.0, 147.4, 138.3, 133.8, 132.7, 132.1, 131.7, 130.5, 129.7, 127.6, 126.9, 123.8, 121.7, 121.2, 116.2, 111.3, 110.6, 54.7 ppm; mass (ES^+) *m/z* 377.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}Cl_3N_2O$: C, 57.25; H, 2.94; N, 7.42; Found: C, 57.28; H, 2.93; N, 7.40.

7-chloro-11-(3,4-dichlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6e):
Yield = 0.225 g (88%), yellow solid, mp 161-162°C, R_f = 0.46 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3315, 1627, 1605, 1477, 1406, 1312, 1122 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 8.34 (1H, d, *J* = 2.6 Hz, ArH), 7.68-7.66 (1H, m, ArH), 7.49-7.46 (2H, m, ArH), 7.32 (1H, dd, *J* = 8.6, 2.6 Hz, ArH), 7.20 (1H, dd, *J* = 8.3, 2.0 Hz, ArH), 7.73 (1H, d, *J* = 8.7 Hz, ArH), 6.22 (1H, d, *J* = 3.3 Hz, ArH), 5.58-5.57 (1H, m, ArH), 5.35 (1H, s, CH), 4.80 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 162.6, 147.3, 138.9, 134.9, 133.8, 133.3, 133.1, 132.9, 131.1,129.9, 127.3, 125.6, 123.1, 121.2, 117.4, 112.1, 112.0, 57.9 ppm; mass (ES^+) *m/z* 377.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}Cl_3N_2O$: C, 57.25; H, 2.94; N, 7.42; Found: C, 57.27; H, 2.91; N, 7.43.

4-(7-chloro-5-oxo-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-11-yl)benzonitrile (6f):
Yield = 0.198 g (87%), yellow solid, mp 181-182°C, R_f = 0.50 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3332, 1783, 1649, 1484, 1306, 1122 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.30 (1H, d, *J* = 2.5 Hz, ArH), 7.70-7.67 (3H, m, ArH), 7.46 (2H, d, *J* = 8.3 Hz, ArH), 7.33 (1H, dd, *J* = 8.6, 2.5 Hz, ArH), 6.77 (1H, d, *J* = 8.6 Hz, ArH), 6.25 (1H, d, *J* = 3.3 Hz, ArH), 5.60 (1H, d, *J* = 1.9 Hz, ArH), 5.50 (1H, d, *J* = 2.0 Hz, ArH), 5.93 (1H, s, ArH), 5.01 (1H, d, *J* = 1.9 Hz, NH); ^{13}C NMR (50 MHz, $CDCl_3$+DMSO-d_6) δ = 161.9, 146.9, 144.3, 133.8, 132.0, 131.5, 130.9, 127.8, 122.9, 121.6, 121.0, 117.7, 115.3, 111.2, 110.9, 110.8, 55.3 ppm; mass (ES^+) *m/z* 334.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{12}ClN_3O$: C, 68.37; H, 3.62;; N, 12.59; Found: C, 68.39; H, 3.60; N, 12.58.

7-chloro-11-(4-fluorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6g):
Yield = 0.162 g (73%), yellow solid, mp 172-173°C, R_f = 0.38 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3361, 1641, 1497, 1315, 1161 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.36 (1H, d, *J* = 2.5 Hz, ArH), 7.67-7.41 (1H, m, ArH), 7.41-7.37 (2H, m, ArH), 7.30 (1H, dd, *J* = 8.6, 2.5 Hz, ArH), 7.14-7.08 (2H, m, ArH), 7.70 (1H, d, *J* = 7.3 Hz ArH), 6.20 (1H, t, *J* = 3.3 Hz, ArH), 5.48-5.46 (1H, m, ArH), 5.34 (1H, s, CH), 4.74 (1H, brss, NH); ^{13}C NMR (50 MHz, $CDCl_3$+DMSO-d_6) δ = 162.7, 147.8, 134.7, 134.2, 133.8, 129.9, 125.4, 122.9, 121.1, 117.3, 116.3, 115.9, 111.9, 111.8, 58.4 ppm; mass (ES^+) *m/z* 327.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}ClFN_2O$: C, 66.16; H, 3.70; N, 8.57; Found: C, 66.15; H, 3.72; N, 8.55.

7-chloro-11-(4-methylphenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (6h):
Yield = 0.123 g (56%), yellow solid, mp 159-161°C, R_f = 0.42 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3341, 1627, 1486, 1414, 1311, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.37 (1H, d, *J* = 2.5 Hz, ArH), 7.66-7.64 (1H, m, ArH), 7.31-7.21 (5H, m, ArH), 6.67 (1H, d, *J* = 8.6, Hz, ArH), 6.18 (1H, t, *J* = 3.3 Hz, ArH), 5.48-5.47 (1H, m, ArH), 5.29 (1H, s, CH), 4.74 (1H, brs, NH), 4.74 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$+DMSO-d_6) δ = 162.9, 148.2, 138.9, 135.8, 134.8, 134.6, 133.8, 129.8, 127.9, 125.1, 122.7, 121.0, 117.2, 111.8, 111.6, 58.9, 58.4 ppm; mass (ES^+) *m/z* 323.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{15}ClN_2O$: C, 70.70; H, 4.68; N, 8.68; Found: C, 70.73; H, 4.65; N, 8.67.

8-chloro-11-(4-chlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (7a):
Yield = 0.203 g (87%), yellow solid, mp 144-146°C, R_f = 0.45 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3308, 1627, 1478, 1415, 1322 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.33 (1H, d, *J* = 8.8 Hz, ArH), 7.67-7.66 (1H, m, ArH), 7.41-7.31 (4H, m, ArH), 6.92 (1H, dd, *J* = 8.8, 2.0 Hz, ArH), 6.78 (1H, d, *J* = 1.9 Hz, ArH), 6.20 (1H, t, *J* = 3.3 Hz, ArH), 5.51 (1H, s, ArH), 5.36 (1H, s, CH), 4.79 (1H, brs, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ =163.1, 149.7, 140.9, 137.2, 136.5, 134.8, 133.6, 129.4, 129.3, 122.9, 120.8, 118.8, 114.9, 111.8, 58.2 ppm; mass (ES^+) *m/z* 343.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; Cl, 20.66; N, 8.16; Found: C, 62.97; H, 3.54; N, 8.18.

11-(4-bromophenyl)-8-chloro-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (7b):
Yield = 0.205 g (78%), yellow solid, mp 154-155°C, R_f = 0.40 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3350, 1638, 1478, 1419, 1323 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.33 (1H, d, *J* = 8.8 Hz, ArH), 7.67-7.66 (1H, m, ArH), 7.55 (2H, d, *J* = 8.4 Hz, ArH), 7.27 (2H, d, *J* = 8.4 Hz, ArH), 6.93 (1H, dd, *J* = 8.8, 2.0 Hz, ArH), 6.78 (1H, d, *J* = 1.9 Hz, ArH), 6.20 (1H, t, *J* = 3.3 Hz, ArH), 5.52 (1H, s, ArH), 5.35 (1H, s, CH), 4.79 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.1, 149.7, 140.9, 137.8, 136.5, 133.5, 132.3, 129.7, 122.9, 122.8, 120.8, 118.8, 114.9, 111.8, 58.2 ppm; mass (ES^+) *m/z* 387.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}BrClN_2O$: C, 62.99; H, 3.52; N, 8.16; Found: C, 62.98; H, 3.53; N, 8.15.

8-chloro-11-(4-nitrophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (7c):
Yield = 0.214 g (89%), yellow solid, mp 216-218°C, R_f = 0.50 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3294, 1632, 1480, 1435, 1334 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.30 (1H, d, *J* = 8.9 Hz, ArH), 8.25 (2H, d, *J* = 8.8 Hz, ArH), 7.70-7.68 (1H, m, ArH), 7.50 (2H, d, *J* = 8.6 Hz, ArH), 6.94 (1H, dd, *J* = 9.4, 1.9 Hz, ArH), 6.83 (1H, d, *J* = 1.9 Hz, ArH), 6.24 (1H, t, *J* = 3.3 Hz, ArH), 5.62 (1H, s, ArH), 5.56 (1H, d, *J* = 3.0 Hz, CH), 4.97 (1H, brs, NH); ^{13}C NMR (50 MHz, DMSO-d_6) δ = 162.5, 149.8, 147.2, 146.9, 139.5, 135.5, 131.3, 128.5, 123.6, 121.8, 118.6, 113.0, 111.9, 111.5, 54.1 ppm; mass (ES^+) *m/z* 354.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}ClN_3O_3$: C, 61.11; H, 3.42; N, 11.88; Found: C, 61.14; H, 3.41; N, 11.86.

4-(8-chloro-5-oxo-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-11-yl)benzonitrile (7d):
Yield = 0.175 g (77%), white solid, mp 184-186°C, R_f = 0.40 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3328, 1647, 1483, 1402, 1326 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.28 (1H, d, *J* = 8.8 Hz, ArH), 7.68-7.66 (3H, m, ArH), 7.45 (2H, d, *J* = 8.2 Hz, ArH), 6.92 (1H, dd, *J* = 8.8, 1.9 Hz, ArH), 6.83 (1H, d, *J* = 1.9 Hz, ArH), 6.23 (1H, t, *J* = 3.3 Hz, ArH), 5.60 (1H, d, *J* = 1.9 Hz, ArH), 5.50 (1H, d, *J* = 2.3 Hz, CH), 5.03 (1H, d, *J* = 2.0 Hz, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 162.8, 149.1, 143.9, 141.1, 136.5, 132.8, 132.1, 128.7, 123.1, 121.0, 118.9, 118.3, 115.0, 112.7, 112.0, 111.8, 57.9 ppm; mass (ES^+) *m/z* 334.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{12}ClN_3O$: C, 68.37; H, 3.62; N, 12.59; Found: C, 68.34; H, 3.63; N, 12.61.

9-chloro-11-(4-chlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8a):
Yield = 0.166 g (71%), yellow solid, mp 128-129^{o}C, R_f = 0.39 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3373, 1675, 1597, 1489, 1397, 1319 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.31 (1H, dd, *J* = 8.3, 1.4 Hz, ArH), 7.66-7.65 (1H, m, ArH), 7.51 (1H, dd, *J* = 7.7, 1.6 Hz, ArH), 7.36 (2H, dd, *J* = 6.6, 1.9 Hz, ArH), 7.27 (2H, d, *J* = 8.5 Hz, ArH), 6.88 (1H, t, *J* = 7.7 Hz, ArH), 6.23 (1H, t, *J* = 3.3 Hz, ArH), 5.77 (1H, s, CH), 5.65-5.64 (1H, m, ArH), 5.46 (1H, d, *J* = 8.5 Hz, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.1, 144.8, 137.3, 134.7, 134.5, 133.9, 133.5, 129.4, 129.1, 123.0, 122.9, 119.7, 117.9, 111.9, 111.6, 57.6 ppm; mass (ES$^+$) *m/z* 343.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16; Found: C, 62.97; H, 3.53; N, 8.15.

9-chloro-11-(4-nitrophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8b):
Yield = 0.197 g (82%), yellow solid, mp 146-147^{o}C, R_f = 0.40 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3389, 1651, 1597, 1510, 1414, 1327 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.26 (1H, dd, *J* = 7.0, 1.3 Hz, ArH), 8.17 (2H, d, *J* = 8.7 Hz, ArH), 7.69-7.67 (1H, m, ArH), 7.52 (1H, dd, *J* = 7.6, 1.5 Hz, ArH), 7.40 (2H, d, *J* = 8.6 Hz, ArH), 6.87 (1H, t, *J* = 8.0 Hz, ArH), 6.29 (1H, t, *J* = 3.3 Hz, ArH), 5.98 (1H, d, *J* = 3.8 Hz, CH), 5.81 (1H, t, *J* = 2.1 Hz, ArH), 5.69 (1H, d, *J* = 3.8 Hz, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.7, 147.8, 145.9, 143.8, 134.6, 133.9, 131.6, 130.5, 128.4, 124.3, 124.1, 123.1, 123.0, 119.9, 117.9, 112.0, 111.9, 56.9 ppm; mass (ES$^+$) *m/z* 354.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}ClN_3O_3$: C, 61.11; H, 3.42; N, 11.88; Found: C, 61.13; H, 3.41; N, 11.87.

11-(4-bromophenyl)-9-chloro-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8c):
Yield = 0.195 g (74%), yellow solid, mp 133-134^{o}C, R_f = 0.48 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3372, 1672, 1596, 1487, 1319 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.28 (1H, dd, *J* = 8.4, 1.4 Hz, ArH), 7.63-7.62 (1H, m, ArH), 7.50-7.46 (3H, m, ArH), 7.18 (2H, d, *J* = 8.4, Hz, ArH), 6.85 (1H, t, *J* = 7.8 Hz, ArH), 6.20 (1H, t, *J* = 3.3 Hz, ArH), 5.75 (1H, d, *J* = 2.1 Hz, CH), 5.63-5.61 (1H, m, ArH), 5.42 (1H, d, *J* = 2.7 Hz, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.4, 145.1, 138.1, 134.8, 134.3, 133.6, 132.6, 129.6, 123.2, 119.9, 118.3, 112.3, 111.9, 57.9 ppm; mass (ES$^+$) *m/z* 387.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}BrClN_2O$: C, 55.77; H, 3.12; N, 7.23; Found: C, 55.74; H, 3.13; N, 7.25

4-(9-chloro-5-oxo-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-11-yl)benzonitrile (8d):
Yield = 0.179 g (79%), yellow solid, mp 138-139^{o}C, R_f = 0.36 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3370, 2927, 1649, 1505, 1417, 1315, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.28 (1H, dd, *J* = 8.5, 1.4, Hz, ArH), 7.69-7.63 (3H, m, ArH), 7.53 (1H, dd, *J* = 7.7, 1.6 Hz, ArH), 7.36 (2H, d, *J* = 8.1 Hz, ArH), 6.91-6.86 (1H, m, ArH), 6.28 (1H, t, *J* = 3.3 Hz, ArH), 5.91 (1H, d, *J* = 3.5 Hz, NH), 5.78-5.76 (1H, m, ArH), 5.63 (1H, d, *J* = 3.8 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.8, 144.1, 144.0, 134.7, 1.34.0, 133.0, 132.8, 131.9, 128.3, 123.1, 123.0, 119.9, 118.4, 118.1, 112.6, 112.0, 111.9, 57.3 ppm; mass (ES$^+$) *m/z* 334.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{12}ClN_3O$: C, 68.37; H, 3.62; N, 12.59; Found: C, 68.35; H, 3.63; N, 12.57.

9-chloro-11-(4-fluorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8e):
Yield = 0.167 g (75%), yellow solid, mp 104-105^{o}C, R_f = 0.43 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3368, 1680, 1598, 1497, 1318 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.35 (1H, dd, *J* = 8.3, 1.4 Hz, ArH), 7.68-7.67 (1H, m, ArH), 7.53 (1H, dd, *J* = 7.6, 1.6 Hz, ArH), 7.37-7.33 (2H, m, ArH), 7.13-7.08 (2H, m, ArH), 6.90 (1H, t, *J* = 8.0 Hz, ArH), 6.25 (1H, t, *J* = 3.3 Hz, ArH), 5.77 (1H, brs, NH), 5.63 (1H, t, *J* = 2.0 Hz, ArH), 5.47 (1H, d, *J* = 2.1 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.3, 163.1, 160.3, 144.9, 134.6, 134.5, 134.4, 133.9, 129.5, 129.4, 122.9, 122.8, 119.6, 117.8, 116.3, 115.9, 111.9, 111.5, 57.6 ppm; mass (ES$^+$) *m/z* 327.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{12}ClFN_2O$: C, 66.16; H, 3.70; N, 8.57; 4.90; Found: C, 66.15; H, 3.71; N, 8.56;

9-chloro-11-(4-methylphenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8f):
Yield = 0.127 g (58%), yellow solid, mp 107-109^{o}C, R_f = 0.56 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3381, 2906, 1662, 1451, 1322 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.33 (1H, dd, *J* = 8.4, 1.5 Hz, ArH), 7.65-7.63 (1H, m, ArH), 7.50 (1H, dd, *J* = 7.6, 1.5 Hz, ArH), 7.28-7.19 (4H, m, ArH), 6.86 (1H, t, *J* = 8.0 Hz, ArH), 6.21 (1H, t, *J* = 3.3 Hz, ArH), 5.76 (1H, brs, NH), 5.58 (1H, d, *J* = 1.9 Hz, ArH), 5.39 (1H, s, CH), 2.38 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.3, 145.4, 138.7, 135.7, 134.6, 134.4, 133.9, 133.5, 130.3, 129.8, 127.6, 122.6, 119.3, 117.7, 113.2, 111.9, 111.3, 58.2, 21.3 ppm; mass (ES^+) *m/z* 323.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{15}ClN_2O$: C, 70.70; H, 4.68; N, 8.68; Found: C, 70.74; H, 4.66; N, 8.66.

9-chloro-11-(3,4-dichlorophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8g):
Yield = 0.205 g (80%), yellow solid, mp 128-130^{o}C, R_f = 0.71 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3375, 1661, 1594, 1454, 1326 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.31 (1H, dd, *J* = 9.1, 1.4 Hz, ArH), 7.68-7.66 (1H, m, ArH), 7.53 (1H, dd, *J* = 7.6, 1.6 Hz, ArH), 7.46-7.39 (2H, m, ArH), 7.14 (1H, dd, *J* = 8.3, 1.9 Hz, ArH), 6.89 (1H, t, *J* = 8.0 Hz, ArH), 6.26 (1H, t, *J* = 3.3 Hz, ArH), 5.77 (1H, d, *J* = 2.3 Hz, NH), 5.72-5.71 (1H, m, ArH), 5.47 (1H, d, *J* = 2.7 Hz, CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 162.9, 144.3, 139.0, 134.6, 134.0, 133.4, 133.0, 132.6, 131.1, 129.7, 126.9, 123.1, 123.0, 119.9, 118.1, 112.0, 111.8, 57.2 ppm; mass (ES^+) *m/z* 377.1 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}Cl_3N_2O$: C, 57.25; H, 2.94; N, 7.42; Found: C, 57.28; H, 2.93; N, 7.40.

9-chloro-11-(4-methylphenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (8h)
Yield = 0.213 g (83%), yellow solid, mp 115-117^{o}C, R_f = 0.43 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3360, 1661, 1594, 1497, 1427, 1322 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.32 (1H, dd, *J* = 8.3, 1.3 Hz, ArH), 7.73-7.72 (1H, m, ArH), 7.49-7.43 (2H, m, ArH), 7.29-7.15 (2H, m, ArH), 6.90-6.84 (1H, m, ArH), 6.26 (1H, t, *J* = 3.3 Hz, ArH), 6.01 (1H, s, ArH), 6.00 (1H, s, CH), 5.70 (1H, brs, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.1, 144.4, 139.1, 134.7, 134.1, 133.8, 131.8, 131.5, 130.7, 127.8, 127.4, 123.4, 123.0, 119.9, 118.3, 112.3, 111.5, 55.5 ppm; mass (ES^+) *m/z* 323.1 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}Cl_3N_2O$: C, 57.25; H, 2.94; N, 7.42;; Found: C, 57.23; H, 2.92; N, 7.44.

11-(4-chlorophenyl)-7-methoxy-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (9a):
Yield = 0.167 g (71%), yellow solid, mp 130-132^{o}C, R_f = 0.60 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3458, 3413,3021, 2925, 2360, 1656, 1505, 1424, 1311 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.55-7.33 (5H, m, ArH), 7.12-7.05 (4H, m, ArH), 6.30 (1H, s, ArH), 5.95 (1H, s, NH), 5.65 (1H, s, CH), 3.68 (3H, s, OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6 + $CDCl_3$); δ = 163.1, 151.6, 144.1, 138.9, 133.0, 132.0, 129.2, 128.2, 124.6, 121.7, 121.4, 114.4, 113.6, 111.5, 110.5, 55.1, 54.8 ppm; mass (ES^+) *m/z* 339.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{15}ClN_2O_2$: C, 67.36; H, 4.46; N, 8.27; Found: C, 67.39; H, 4.44; N, 8.28.

7-methoxy-11-(4-nitrophenyl)-10,11-dihydro-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (9b):
Yield = 0.186 g (77%), yellow solid, mp > 250 ^{o}C, R_f = 0.46 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3293, 3022, 2927, 2361, 1617, 1516, 1423, 1330, 1347 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.15 (2H, d, *J* = 6.5 Hz, ArH), 7.63 (1H, d, *J* = 3.8 Hz, ArH), 7.59 (1H, d, *J* = 1.4 Hz, ArH), 7.46 (1H, d, *J* = 2.0 Hz, ArH), 7.34 (2H, d, *J* = 6.5 Hz, ArH), 7.11-7.04 (2H, m, ArH), 6.35 (1H, t, *J* = 2.4 Hz, ArH), 6.07 (1H, brs, NH), 5.87 (1H, d, *J* = 3.7 Hz, ArH), 3.67 (3H, s, OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 162.9, 151.7, 147.9, 146.8, 143.7, 132.1, 128.6, 124.5, 123.4, 121.8, 121.7, 114.5, 113.7, 111.7, 110.9, 55.1, 54.8 ppm; mass (ES^+) *m/z* 350.2 (M^+ + 1); Anal. Calcd for $C_{19}H_{15}N_3O_4$: C, 65.32; H, 4.33; N, 12.03; Found: C, 65.33; H, 4.35; N, 12.05.

General procedure for the DDQ oxidation:

A mixture of substrate of **Table 3** (0.100g) and DDQ (3.0eq) were treated in dry DCM (5 mL). The reaction mixture was allowed to stir at rt for 15 min. After completion of reaction, the reaction mixture was washed with aq. $NaHCO_3$ (3x30 mL) and extracted with DCM (2x30 mL). The combined organic layer was washed with excess brine water and dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by washing with diethylether (2x20 mL) to afford **10a-k**.

11-(4-chlorophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10a):
Yield = 0.086 g (87%), light yellow solid, mp 175-177^{o}C, R_f = 0.72 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3306, 1630, 1488, 1409, 1318 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 (1H, dd, *J* = 8.1, 1.4 Hz, ArH), 8.24 (1H, dd, *J* = 2.8, 2.1 Hz, ArH), 7.86 (1H, td, *J* = 7.5, 1.4 Hz, ArH), 7.78-7.76 (3H, m, ArH), 7.60-7.55 (3H, m, ArH), 7.83-7.79 (2H, m, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 163.3, 155.5, 145.6, 140.7, 135.4, 134.9, 133.4, 132.7, 131.7, 128.5, 128.0, 127.7, 126.2, 124.6, 121.9, 114.6 ppm; mass (ES$^+$) *m/z* 307.3 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}ClN_2O$: C, 70.48; H, 3.61; N, 9.13; Found: C, 70.46; H, 3.60; N, 9.16.

11-(4-bromophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10b):
Yield = 0.09 g (88%), light brown solid, mp 163-164^{o}C, R_f = 0.64 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3429, 1673, 1579, 1427, 1323 cm^{-1};^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.40 (1H, dd, *J* = 8.4, 1.2 Hz, ArH), 8.22 (1H, d, *J* = 1.8 Hz, ArH), 7.84-7.83 (2H, m, ArH), 7.74-7.66 (4H, m, ArH), 7.56-7.55 (1H, m, ArH), 6.80-6.78 (2H, m, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 163.3, 155.6, 145.6, 141.0, 135.4, 133.4, 132.7, 131.9, 131.4, 129.6, 128.0, 127.7, 126.2, 124.6, 123.7, 121.9, 114.6, 113.2 ppm; mass (ES$^+$) *m/z* 351.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}BrN_2O$: C, 61.56; H, 3.16; N, 7.98; Found: C, 61.58; H, 3.15; N, 7.97.

11-(4-fluorophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10c):
Yield = 0.08 g (81%), white solid, mp 171-172^{o}C, R_f = 0.68 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3448, 1657, 1427, 1330 cm^{-1};^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.40 (1H, d, *J* = 7.8 Hz, ArH), 8.21 (1H, s, ArH), 7.84-7.74 (4H, m, ArH), 7.54 (1H, t, *J* = 7.2 Hz, ArH), 7.33-7.31 (2H, m, ArH), 6.79 (2H, s, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 164.2, 163.4, 155.6, 145.7, 138.3, 135.4, 133.3, 132.6, 132.3, 132.2, 127.9, 126.1, 124.6, 121.9, 115.4, 115.3, 114.5, ppm; mass (ES$^+$) *m/z* 291.2 (M^+ + 1); Anal. Calcd for $C_{18}H_{11}FN_2O$: C, 74.47; H, 3.82; N, 9.65; Found: C, 74.44; H, 3.84; N, 9.66.

11-(2,3-dichlorophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10d):
Yield = 0.083 g (84%), yellow solid, mp 148-150^{o}C, R_f = 0.52 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3423, 1676, 1581, 1421, 1320 cm^{-1};^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.55 (1H, d, *J* = 8.4 Hz, ArH), 8.32-8.31 (1H, m, ArH), 7.90-7.75 (1H, m, ArH), 7.78-7.74 (2H, m, ArH), 7.65-7.63 (1H, m, ArH), 7.57-7.56 (1H, m, ArH), 7.52-7.50 (1H, m, ArH), 7.49-6.78 (1H, m, ArH), 6.54-6.53 (1H, m, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 162.4, 153.6, 145.4, 142.5, 135.8, 134.1, 133.3, 132.4, 131.2, 130.2, 129.3, 128.9, 128.8, 127.8, 126.9, 124.7, 121.6, 115.4 ppm; mass (ES$^+$) m/z 341.3 (M^+ + 1); Anal. Calcd for $C_{18}H_{10}Cl_2N_2O$: C, 63.36; H, 2.95; N, 8.21; Found: C, 63.33; H, 2.92; N, 8.19.

7-methyl-11-(4-nitrophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10e):
Yield = 0.086 g (87%), green solid, mp 172-174^{o}C, R_f = 0.60 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3438, 1664, 1520, 1427, 1344 cm^{-1};^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.36 (2H, d, *J* = 8.8 Hz, ArH), 8.29-8.27 (2H, m, ArH), 7.99-7.96 (2H, m, ArH), 7.71(2H, s, ArH), 6.83-6.77 (2H, m, ArH), 2.5 (3H, s, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 162.9, 153.9, 148.3, 148.0, 143.4, 138.4, 136.4, 133.9,

132.6, 131.1, 127.6, 126.3, 124.3, 123.7, 121.4, 114.7, 21.0 ppm; mass (ES^+) m/z 332.2 ($M^+ + 1$); Anal. Calcd for $C_{19}H_{13}N_3O_3$: C, 68.88; H, 3.95; N, 12.68; Found: C, 68.83; H, 3.96; N, 12.69;.

11-(4-chlorophenyl)-7-methyl-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10f):
Yield = 0.082 g (83%), brown solid, mp 171-173°C, R_f = 0.56 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3428, 1663, 1419, 1326 cm^{-1};^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.24-8.22 (2H, m, ArH), 7.75 (2H, d, *J* = 8.5 Hz, ArH), 7.67 (2H, s, ArH), 7.57 (2H, d, *J* = 8.5 Hz, ArH), 6.80 (2H, d, *J* = 2.5 Hz, ArH), 2.47 (3H, s, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 163.2, 154.6, 143.6, 140.7, 137.8, 136.4, 134.8, 133.6, 132.4, 131.7, 128.5, 127.8, 126.0, 124.2, 121.4, 114.5, 21.2 ppm; mass (ES^+) m/z 321.1 ($M^+ + 1$); Anal. Calcd for $C_{19}H_{13}ClN_2O$: C, 71.14; H, 4.08; N, 8.73; Found: C, 71.16; H, 4.07; N, 8.72.

7-chloro-11-(4-nitrophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10g):
Yield = 0.078 g (79%), yellow solid, mp 198-200°C, R_f = 0.64 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3422, 1664, 1571, 1519, 1423 cm^{-1};^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.40-8.35 (3H, m, ArH), 8.32-8.30 (1H, m, ArH), 7.99-7.91 (3H, m, ArH), 7.80 (1H, d, *J* = 8.6 Hz, ArH), 6.87-6.83 (2H, m, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 161.9, 155.3, 148.4, 147.8, 144.3, 136.0, 135.2, 132.4, 131.7, 131.1, 127.7, 126.9, 125.4, 123.8, 123.3, 115.2, 110.0 ppm; mass (ES^+) m/z 352.2 ($M^+ + 1$); Anal. Calcd for $C_{18}H_{10}ClN_3O_3$: C, 61.46; H, 2.87; N, 11.95; Found: C, 61.43; H, 2.89; N, 11.96.

8-chloro-11-(4-nitrophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10h):
Yield = 0.094 g (92%), light yellow solid, mp 172-173°C, R_f = 0.63 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3446, 1672, 1577, 1433, 1310 cm^{-1};^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.43 (1H, d, *J* = 8.4 Hz, ArH), 8.30 (1H, t, *J* = 2.1 Hz, ArH), 7.99 (2H, d, *J* = 8.4 Hz, ArH), 7.92-7.82 (3H, m, ArH) 7.66 (1H, dd, *J* = 9.1, 2.1 Hz, ArH), 6.84 (2H, d, *J* = 2.7 Hz, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 162.2, 156.5, 146.5, 145.8, 139.8, 134.8, 132.6, 132.5, 130.7, 128.1, 127.0, 125.7, 120.8, 119.0, 115.0, 112.8 ppm; mass (ES^+) *m/z* 352.3 ($M^+ + 1$); Anal. Calcd for $C_{18}H_{10}ClN_3O_3$: C, 61.46; H, 2.87; N, 11.95; Found: C, 61.48; H, 2.86; N, 11.94.

9-chloro-11-(4-nitrophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10i):
Yield = 0.078 g (76%), yellow solid, mp 150-151°C, R_f = 0.59 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3448, 1670, 1582, 1423, 1326 cm^{-1};^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.37 (2H, d, *J* = 8.8 Hz, ArH), 8.33-8.31 (1H, m, ArH), 8.21 (1H, t, *J* = 7.5, 1.8 Hz, ArH), 8.07-8.03 (3H, m, ArH), 7.53 (1H, t, 7.8 Hz, ArH), 6.91-6.82 (2H, m, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 162.9, 155.1, 148.8, 147.3, 141.5, 135.9, 135.8, 131.8, 131.6, 128.5, 127.4, 126.6, 124.7, 124.5, 123.8, 114.9 ppm; mass (ES^+) *m/z* 352.1 ($M^+ + 1$); Anal. Calcd for $C_{18}H_{10}ClN_3O_3$: C, 61.46; H, 2.87; N, 11.95; Found: C, 61.48; H, 2.86; N, 11.94.

4-(9-chloro-5-oxo-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-11-yl)benzonitrile (10j):
Yield = 0.091 g (92%), white solid, mp 214-216°C, R_f = 0.62 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3422, 1661, 1591, 1427, 1322 cm^{-1};^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.32 (1H, dd, *J* = 8.1, 1.6 Hz, ArH), 8.22-8.20 (1H, m, ArH), 8.05-8.01 (5H, m, ArH), 7.53 (1H, t, *J* = 7.9 Hz ,ArH), 6.91-6.89 (1H, m, ArH), 6.83 (1H, t, *J* = 3.4 Hz, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 162.9, 155.4, 145.6, 141.6, 135.9, 135.7, 132.6, 131.6, 131.3, 128.4, 127.3, 126.5, 124.6, 124.5, 118.9, 114.8, 113.2 ppm; mass (ES^+) m/z 332.3 ($M^+ + 1$); Anal. Calcd for $C_{19}H_{10}ClN_3O$: C, 68.79; H, 3.04; N, 12.67; Found: C, 68.76; H, 3.06; N, 12.68.

9-chloro-11-(3,4-dichlorophenyl)-5*H*-pyrrolo[2,1-*c*][1,4]benzodiazepin-5-one (10k):
Yield = 0.075 g (76%), light green solid, mp 167-169°C, R_f = 0.47 (2:8 EtOAc:Hexane), IR (KBr) ν_{max} 3413, 1668, 1443 cm^{-1};^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.30 (1H, dd, *J* = 7.3, 1.6 Hz, ArH), 8.20-

8.18 (1H, m, ArH), 8.08-8.02 (2H, m, ArH), 7.82 (2H, s, ArH), 7.53 (1H, t, *J* = 7.7 Hz, ArH), 7.01-6.98 (1H, m, ArH), 6.85-6.82 (1H, m, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 163.1, 154.5, 141.8, 141.5, 135.9, 135.5, 133.7, 132.2, 131.5, 131.4, 130.9, 130.7, 128.3, 127.1, 126.5, 124.6, 124.5, 114.8 ppm; mass (ES^+) *m/z* 375.1 (M^+ + 1); Anal. Calcd for $C_{18}H_9C_{l3}N_2O$: C, 57.55; H, 2.41; N, 7.46; Found: C, 57.58; H, 2.40; N, 7.44.

Acknowledgments:

The authors would like to thank SAIF, Lucknow, India for providing spectral data. S.K.S and A.K.M. are grateful to CSIR, New Delhi, India for research fellowship whereas K.K. is grateful to Indian Academy of Sciences Bangalore, India for being awarded summer fellowship.

References:

1) CDRI Communication Number 7931

2) (a) Jetze J, T. *Current Bioactive Compounds* **2009**, *5*, 1-1. (b) Kaisera, M.; Wetzelb, S.;. Kumarb, c, K.; Waldmannb, c, H. *Cell. Mol. Life Sci.* **2008**, *65*, 1186–1201. (c) Newman, D. J.; Cragg, G. M. *J. Nat. Prod.* **2007**, *70*, 461–477.(d) Nçren-Müller, A.; Reis-CorrÞa, I.; Prinz, Jr., H.; Rosenbaum, C.; Saxena, K.; Schwalbe, H.; Vestweber, D.; Cagna, G.; Schunk, S.; Schwarz, O.; Schiewe, H.; Waldmann, H. *Proc. Natl. Acad. Sci. USA.* **2006**, *103*, 10606–10611. (e) Koch, M. A.; Schuffenhauer, A.; Scheck, M.; Wetzel, Casaulta, S. M.; Odermatt., A.; Ertl, P.; Waldmann, H. *Proc.Natl. Acad. Sci. USA* **2005**, *102*, 17272–17277. (f) Shang, S.; Tan, D. S. *Curr. Opin. Chem. Biol*. **2005**, *9*, 248–258. (g) Frank, R. *Curr. Opin. Biotechnol.* **2004**, *15*, 573–575. (h) Schreiber, S. L. *Target-oriented and diversity-oriented organic. 1 synthesis in drug discovery.Science*, **2000**, *287*, 1964-1969. (i) Liu, D. R.; Schultz, P. G. *Angew Chem Int Ed Engl.* **1999**, *38*, 36-54. (j) Nicolaou, K. C.; Pfefferkorn, J. A.; Roecker, A. J.; Cao, G. Q.; Barluenga, S.; Mitchell, H. J. *J Am Chem Soc* **2000**, *122*, 9939-9953.

3) (a) Hong, B.C.; Nimje, R.Y. *Current Organic Chemistry* **2006**, *10*, 2191-2225. (b) Brown, J. M.; Cooley, N. A. *Chem. Rev.*, **1988**, *88,* 1031–1046.

4) Agarwal, P. K.; Sawant, D.; Sharma, S.; Kundu, B. *Eur J Org Chem*., **2009**, *2*, 292-303.

5) Mandadapu, A. K.; Saifuddin, M.; Agarwal, P. K.; Kundu, B. *Org. Biomol. Chem*., **2009**, *7*, 2796–2803.

6) Agarwal, P. K.; Sawant, D.; Sharma, S.; Kundu, B. *Eur J Org Chem*., **2009**, *2*, 292-303.

7) Komatsu, N.; Kimura, K.; Abe, S.; Kagitani, Y. *J. Antibiot.* **1980**, *33*, 54–60.

8) Arima, K.; Kosaka, M.; Tamura, G.; Imanaka, H.; Sakai, H. *J. Antibiot*. **1972**, *25*, 437–444

9) Shimizu, K.; Kawamoto, I.; Tomita, F.; Morimoto, M.; Fujimoto, K. *J. Antibiot*. **1982**, *35*, 972–978.

10) Brazhnikova, M. G.; Konstantinova, N. V.; Mesentsev, A. S. *J. Antibiot*. **1972**, *25*, 668–673.

11) Mohr, N.; Budzikiewicz, H. *Tetrahedron* **1982**, *38*, 147-152.

12) Rahbaek, L.; Breinholt, J.; Frisvad, J. C.; Christophersen, C. *J. Org.Chem*. **1999**, *64*, 1689-1692.

13) (a) Denny, W. A. *Curr. Med. Chem.* **2001**, *8*, 533–544.(b) Hadjivassileva, T.; Thurston, D. E.; Taylor, P. W.; *J. Antimicrob. Chemother.* **2005**, *56*, 513–518.

14) (a) Thurston, D. E. *Br. J. Cancer* **1999**, *80*, 65–85 (b) Kamal, A.; Rao, M. V.; Laxman, N.; Ramesh, G.; Reddy, G. S. *Curr. Med. Chem. Anticancer Agents* **2002**, *2*, 215–254 (c) Antonow, D.; Barata, T.; Jenkins, T.C.; Parkinson, G. N.; Howard, P. W.; Thurston, D. E.; Zloh, M. *Biochemistry.* **2008,** *47*, 11818–11829.

15) (a) Kaneko, T.; Wong, H.; Doyle, T. W. *J. Antibiot*. **1984**, *37*, 300–302. (b) Clark, R. L.; Carter, K. C.;.Mullen, A. B.; Coxon, G. D.; Owusu-Dapaah, G.; McFarlane, E.; Duong Thi, M. D.; Grant, M. H.; Tettey, J. N.; Mackay, S. P. *Bioorg. Med. Chem. Lett*. **2007**, *17*, 624–627. (c) Guaciaro, M. A.; Harrington, P. M.; Karp, G. M.; U.S. *Patent 5438035 A 19950801,* **1995**.

16) Fotso, S.; Zabriskie, T. M.; Proteau, P. J.; Flatt, P. M.; Santosa, D.A.; Sulastri, Mahmu, T. *J. Nat. Prod*. **2009**, *72*, 690–695.

17 (a) Albright, Jay D.; Reich, Marvin F.; Sum, Fuk-Wah; Delos Santos, Efren Guillermo. (American Cyanamid Co., USA). Eur. Pat. Appl. (1995), 256 pp.

18) (a) Hu, W. P.; Wang, J. J.; Lin, F. L.; Lin, Y. C.; Lin, S. R.; Hsu, M. H. *J. Org. Chem.* **2001**, *66,* 2881-2883. (b) Gil, C.; Brase, S. *Chem. Eur. J.* **2005**, *11*, 2680 – 2688. (c) Masterson, L. A.; Croker. S. J.; Jenkins, T. C.; Howarda, P. W.; Thurstona, D. E. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 901–904. (d) Rahbæk, L.; Breinholt, J. *J. Nat. Prod.* **1999**, *62*, 904-905 (e). Kitamura, T.; Sato, Y.; Mori, M. *Tetrahedron* **2004**, *60*, 9649–9657.(f) Fabis, F.; Santos, J. S. O.; Jolivet, S. F.; Rault, S. *Tetrahedron Letters* **2001**, *42*, 5183–5185 (g) Gillard, A.C.; Fabis, F.; Fouchet, S. J.; Rault, S. *Tetrahedron Letters* **1997**, *38*, 2211-2214. (h) Kamal, A.; Rao M. V.; Reddy, B. S. *Chemistry of Heterocyclic Compounds* **1998**, *34*, 1342-1358. (i) Kamal, A.; Howard, P. W.; Reddy, B. S. N.; Reddy, B. S. P.; Thurston, D. E. *Tetrahedron* **1997**, *53*, 3223-3230. (j) Kraus, G. A.; Melekhov, A. *Tetrahedron* **1998**, *54*, 11749-l 1754. (k) Wells, G.; Martin, C. R. H.; Howard, P. W.; Sands, Z. A.; Laughton, C. A.; Tiberghien, A.; Woo, C. K.; Masterson, L. A.; Stephenson, M. J.; Hartley, J. A.; Jenkins, T. C.; Shnyder, S. D.; Loadman, P.

M.; Waring, M. J.; Thurston, D. E. *J. Med. Chem* **2006**, *49*, 5442-5461. (l) Thurston, D. E.; Bose, D. S. Chem Rev. 1994, 94, 433-465.

19) Parker, K. A.; Fedynyshyn, T. H. *Tetrahedron Letters* **1979**, *19*, 1657-1660.

21) (a) Kundu, B.; Sawant, D.; Chhabra, R. *J. Comb. Chem*. **2005**, *7*, 317-321.(b) Kundu, B.; Sawant, D.; Partani, P.; Kesarwani, A. P. *J. Org. Chem.* **2005**, *70*, 4889-4892. (c) Duggineni, S.; Sawant, D.; Saha,. B.; Kundu, B. *Tetrahedron* **2006**, *62*, 3228-3241. (d) Sharma, S.; Saha, B.; Sawant, D.; Kundu, B. *J. Comb. Chem*. **2007**, *9*, 783-792. (e). Saha, B.; Sharma, S.; Sawant, D.; Kundu, B. *Tetrahedron,* **2008**, *64*, 8676–8684. (f) Agarwal, P. K.; Sharma, S. K.; Sawant, D.; Kundu, B. *Tetrahedron* **2009**, 65, 1153–1161.(g) Sharma, S. K.; Sharma, S.; Agarwal, P. K.; Kundu B. Eur *J Org Chem*. **2009**, 9, 1309-1312. (h) Sharma, S.; Kundu, B. *J. Comb. Chem*. **2009**, 11, 720–731.(i) Agarwal, P. K.; Saifuddin, M.; Kundu, B. *Tetrahedron* **2010**, 66, 862–870.

22) Wingler, F. Methoden *Org. Chem.(Houben-Weyl) 4th ed*. 1952± Vol. 7/. 2a;Georg Thieme Verlag Stuttgart, **1952**, 581. (b) D'Silva, C.; Iqbal, R. Synthesis 1996, 457. .