A Novel synthesis of aryl- and heteroaryl- annulated carbazoles: Newly synthesized pyrido-, benzo[*a*]- and spirooxindolinebenzo[*a*]-carbazols

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Abstract

A previously unknown class of highly substituted aryl- and heteroaryl-annulated carbazoles such as pyrido[2,3-*a*]carbazole, benzo[*a*]carbazole and spiro[indoline-3',4-benzo[*a*]carbazole] has been prepared by the condensation of substituted α,α-dicyanoalkenes and malononitrile with salicylaldehyde, aryl/heteroaryl aldehydes and isatin respectively in good to excellent yield. The structures of the compounds were confirmed spectroscopically (FT-IR, ^{1}H NMR, ^{13}C NMR) and by single X-ray diffraction. The generality and functional tolerance of this convergent method is demonstrated. Compared with the former and contemporary reaction methodologies, these approaches afford several advantages such as operational simplicity, simple work-up procedure, higher yield, short reaction time and environment friendly protocols.

Keywords

α,α-Dicyanoolefins

Malononitrile

Salicylaldehyde

Aryl- and heteroaryl

Ionic liquid [bmim]BF_4

Isatin

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Introduction

Nitrogen-containing heterocycles represent sought after functional motifs in the fields of medicinal chemistry, natural products and functional material sciences.[1] Among them, carbazole alkaloids are a growing class of natural products, which display a wide variety of biological activities, such as antitumor,[2,3] anti-oxidative,[4] antibacterial,[5] anti-inflammatory, anti-TB[6] and anti-mutagenic activities.[7,8] Recently, a number of carbazole-based compounds have been used as organic materials, due to their well-known photo conducting[9] and semiconducting properties,[10] and their charge-transport and high thermal properties.[11] Aryl- and hetero aryl-annulated carbazoles [AHACs] are key constituents found in natural products, biologically active molecules and drugs[12] as well as in optoelectronic materials.[13] AHACs are classified into [a]-, [b]- and [c]- types based on the position at which an aryl or a heteroaryl ring is fused to the carbazole nucleus. AHACs represent an important class of compounds in view of their biological and pharmacological activities that result from their special affinity toward DNA.[14] Pyrido- and benzo- annulated carbazoles are pharmacologically interesting owing to their potential anti-tumour activity due to their planar conformation.

The rich and efficient chemistry that stems from multicomponent reactions (MCRs) provide a convenient approach to pursue the synthesis of heterocyclic compounds.[15] MCRs often shorten reaction periods and give comparatively higher overall chemical yields compared to multistep syntheses, and thus reduce the use of energy and manpower.[16] In recent years, MCRs have been used for the *in situ* generation of dicyanoolefins for the formation of various aryl- and heteroaryl-annulated carbazoles.

α,α-Dicyanoolefins emerged as versatile reactants have been exploited as vinylogous nucleophiles, Michael acceptors and dienophiles in a variety of organic reactions. Over the past five years some significant progress has been achieved by using α,α-dicyanoolefins as vinylogous donors in synthetic chemistry.[17] They are readily prepared by the condensation of carbonyl compounds and malononitrile and the acidity of γ-C-H is greatly enhanced when the strong electron-withdrawing groups (cyano groups) are attached to C=C bonds, which allow the easy generation of nucleophilic species by *in situ* deprotonation under mild conditions.[18] Malononitrile is another most versatile reagent to be used in MCRs because of the high reactivity of both methylene and cyano groups.[19]

Pyridocarbazoles are most imperative heteroannulated carbazoles and these compounds are endowed with a wide array of biological as well as pharmacological activities, particularly anticancer activity based on DNA binding intercalation, inhibition of topoisomerase II, antimalarial and anti-HIV activities.[20-22] Furthermore, the presence of phenolic–OH group attached to the ring structure enhanced the biological activity, particularly the antioxidant activity. The transformation to *o*-hydroxyphenyl substituted pyrido[2,3-*a*]carbazoles performed with the synthon, 1-(α,α-dicyanomethylene)-2,3,4,9-tetrahydro-1*H*-carbazol-1-one, salicyladehyde and malononitrile is especially attractive. Thus, an efficient route for producing pyrido[2,3-*a*]carbazoles, under efficient and mild conditions is highly desirable and also none of the previous strategies have been reported the construction of *o*-hydroxyphenyl substituted pyrido[2,3-*a*]carbazoles, derived from α,α-dicyanoolefins.

Benzo[*a*]carbazoles, a subclass of carbazoles, have drawn significant biological and pharmacological activities which make them attractive scaffolds for both synthetic and medicinal chemists. Although the benzocarbazole core is rarely found in natural products, these structural motifs exhibit considerable biological activities such as antitumor,[23] antifungal,[24] anti-inflammatory[25] and antiestrogenic[26] properties. Recently, several benzocarbazole analogues have also been shown extensive application as photographic materials.[27] Realisation of the potential of benzocarbazoles as both therapeutic agents as well as functional materials has sparked new efforts into finding alternative or more efficient pathways towards the preparation of these compounds. Spiroheterocycles are of considerable interest due to the presence of a spiro carbon atoms which causes structural rigidity owing to conformational restrictions which considerably influences the biological activities.[28] The spiro cyclic oxindole scaffold, of synthetic or natural origin, is endowed with a wide range of bio-, physio-, and pharmaceutical activities.[29] As a privileged scaffold, the spirocyclicoxindole core structure is found in a wide variety of biologically active natural products and medicinally relevant compounds.[30-33] The above mentioned biological importance of spirooxindole and benzocarbazole in conjunction with our interest in the synthesis of novel heterocycles, led us now to report the synthesis of hybrid heterocycles comprising benzocarbazole and spirooxindole moieties. Moreover, spiro[2'-oxoindoline-3',4-benzo[a]carbazole] skeleton seems to be promising candidate by sharing of the indole 3-carbon atom in the formation of spirooxindole derivatives enhancing biological

activities. To the best of our knowledge this is the first report on the synthesis of spirooxindole-benzocarbazole hybrids.

Motivated by the afore-mentioned findings, and in continuation to our efforts to develop new methods for the synthesis of heterocycles[34] through multi-component reactions (MCRs), herein we report the synthesis of pyrido[2,3-*a*]carbazoles, benzo[a]carbazoles and benzocarbazole-spirooxindole derivatives using 1-(dicyanomethylene)-2,3,4,9-tetrahydro-1*H*-carbazol-1-one as vinylogous nucleopliles under mild reaction conditions.

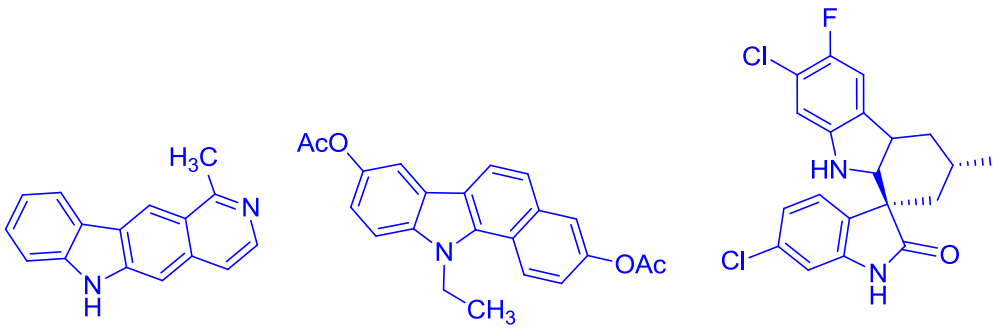
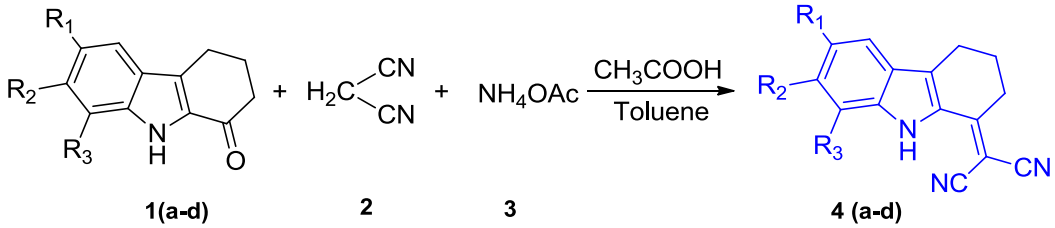


Fig. I. Biologicaly active aryl/heteroaryl annulated carbazole derivetives

Results and discussions

For the synthesis of novel aryl- and heteroaryl-annulated carbazoles, at first we attempted to obtain 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole by the condensation of 2,3,4,9-tetrahydro-1*H*-carbazolone **1** with malononitrile **2** and ammonium acetate **3** in the presence of catalytic quantity of acetic acid in toluene, following procedures found in the literature[35] (**Scheme 1**).



1,4 a: $R_1 = CH_3$, $R_2 = R_3 = H$
b: $R_1 = R_2 = H$, $R_3 = CH_3$
c: $R_1 = Cl$, $R_2 = R_3 = H$
d: $R_1 = R_2 = R_3 = H$

Scheme 1. Synthesis of 1-(dicyanomethylene)-2,3,4,9-tetrahydro-1*H*-carbazole **4**

The structures of all the dicyanoolefins **4 (a-d)** were supported by elemental analysis and spectral data. The FT-IR spectrum of **4a** displayed a characteristic band for cyano groups at 2211 $cm^{-1}$and absorption at 3381 cm^{-1} ascribable to indole NH stretching. The ^{1}H NMR spectrum exhibited a broad singlet at δ 9.25 ppm due to the presence of the indole NH proton. A singlet at δ 7.38 ppm assigned to a proton at C_5 position. Multiplet signals in the region δ 7.30-7.25 ppm arise for the two aromatic protons. The signals due to C_4, C_3 & C_2 aliphatic protons were visible as two multiplets centered at δ 2.97 and 2.09 ppm, and a singlet at δ 2.43 ppm accounted for three methyl protons at C_6 position. The ^{13}C NMR spectrum revealed the presence of 16 carbons. The resonance signals at δ 113.6 and 21.3 were attributed to two cyano and methylcarbons. The identities of the other compounds **4** (**b-d**) were established in a similar ways with all spectroscopic data readily assignable. The structure of one of the members of the series, **4a**, was confirmed by single crystal X-ray diffraction (**Fig. 2**).

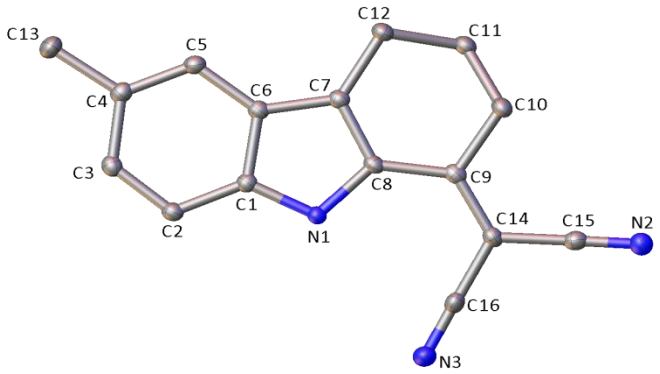
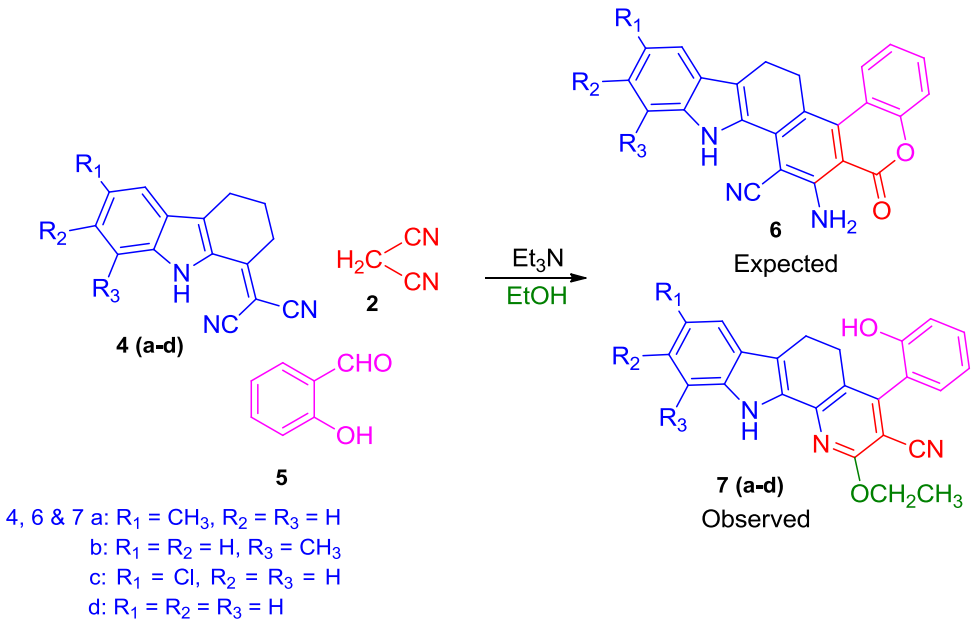


Fig. 2 Structure of **4a** showing the atomic numbering scheme with the thermal ellipsoids depicted at the 50% probability level. Hydrogen atoms are omitted for clarity

With the starting materials in hands, we attempted to synthesis 2-amino-3-imino-3,9,10,15-tetrahydrobenzo[3,4]isochromeno[5,6-*a*]carbazole-1-carbonitrile **6** in a one-step method, as shown in **Scheme 2**. In this method, the synthon 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** was reacted with malononitrile **2** and salicylaldehyde **5** in aqueous EtOH solvent using triethylamine as N-base catalyst under reflux condition to yield a single product. The Infrared FT-IR and ^{1}H NMR spectra of the obtained compounds revealed the absence of cyano, amino and iminogroups. All the spectral details attest that the structure of the obtained compound is 2-ethoxy-4-(2-hydroxyphenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile **7**, not the expected target product **6** (**Scheme 2**).



Scheme 2. Synthesis of 2-ethoxy-4-(2-hydroxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile **7.**

Further, our interest turned to the synthesis of the medicinally active coumarin derivative **6**, but the attempted synthesis yielded the unexpected hydroxyl substituted pyrido[2,3-*a*]carbazoles **7** from dicyanoolefins. In our initial endeavour, we carried out the above reaction using various basic catalysts in different solvents (**Table 1**).

Table 1. Optimization of reaction condition for compound **7** (**a-d**)[a]

Entry	Base	Solvent	Time (h)	Yield (%) [b]
1	-	EtOH	10	-
2	K_2CO_3	EtOH	8	57
3	DABCO	EtOH	8	36
4	NaOEt	EtOH	8	47
5	Piperidine	EtOH	5	52
6	Et_3N	EtOH	3	83
7	Et_3N	CH_3OH	3	63
8	Et_3N	CH_3CN	4	55

[a] Reaction condition: **5** (1.0 mmol), **4** (**a-d**) (1.0 mmol), **2** (1 mmol), Et_3N (0.2 mL), EtOH 15 mL, reflux 2 h. [b] Isolated yields

In the absence of any catalyst we did not observe any of the three component product under reflux condition even after 10 h stirring (Table 1, entry 1). Interestingly when the same reaction was carried out in the presence of potassium carbonate as base in refluxing ethanol the desired product **7a** was obtained in moderate yields (Table 1, entry 2). Encouraged by this result we attempted to optimize this reaction by using different catalysts such as DABCO, NaOEt, piperidine and Et_3N. Among all these, Et_3N was found best in terms of yields obtained and reaction time. We also screened different solvents such as EtOH, MeOH and CH_3CN using Et_3N as base, but in all these cases yields were found lower than in EtOH. The results showed that the best reaction condition for the synthesis of pyrido[2,3-*a*]carbazoles was ethanol as the solvent and Et_3N as the efficient and cheap catalyst under reflux conditions (entry 6). Under these conditions compound **7a** was isolated in nearly 83%, and no side products were observed. As a weak base, triethylamine makes the Knoevenagel condensation and Michael addition reaction for the preparation of pyrido[2,3-*a*]carbazoles with good to excellent yields. This process is very clean and avoids the use of toxic organic solvents, thereby enhancing the greenness of the transformation.

The reaction was found to be general and use of this method with various other substituted 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (**b-d**) gave highly substituted pyrido[2,3-*a*]carbazoles in good yields (**Table 2**).

Table 2. Synthesis of pyrido[2,3-*a*]carbazole **7** (**a-d**).

Entry	R_1	R_2	R_3	Product	Time (h)	Yield (%) [a]
1.	CH_3	H	H	**7a**	3	83
2.	H	H	CH_3	**7b**	3	79
3.	Cl	H	H	**7c**	3.5	73
4.	H	H	H	**7d**	3	80

[a] Isolated product

The IR, ^1H NMR and ^{13}C NMR data, microanalysis and X-ray diffraction studies were used to ascertain the structures of all the products. The IR spectrum of **7a** shows absorption peaks at 3379, 3211, 2228 and 1555 cm^{-1} which attest to the presence of hydroxyl, indole NH, cyano and C=N groups respectively. The ^1H NMR spectra exhibits two broad singlets at δ 10.22 and 9.26 ppm were due to the hydroxyl and indole NH protons respectively, the signals due to

C_{10}-H was visible as a doublet at δ 7.27 (J_o = 7.6 Hz). Multiplet signals in the region δ 7.18-7.16 ppm arise for the two aromatic protons at C_7 and C'_6, and the signal due to C_9-H occurred as a doublet of doublet at δ 7.02 (J_m= 1.6 & J_o=7.6 Hz). The aromatic protons at C'_5, C'_3 and C'_4 appeared as multiplets in the region of δ 6.95-6.82 ppm. The two protons of $OC\mathbf{H_2}CH_3$ appeared as a quartet at δ 4.60 (J = 7.2 Hz). The methylene protons of C_5 and C_6 appeared as a multiplet centered at δ 2.71, and a sharp singlet at δ 2.23 ppm accounted for the three methyl protons at C_8 position. Three protons of $OCH_2C\mathbf{H_3}$ appeared as a triplet at δ 1.39 (J =7.2 Hz). The ^{13}C NMR spectrum of **7a** displayed 25 resonances which in agreement with the proposed structure. A sharp singlet at δ 116.1 corresponding to cyano group carbon. The resonance signals at δ 62.6 and 14.7 were attributed to $O\mathbf{C}H_2CH_3$ and $OCH_2\mathbf{C}H_3$ carbons. The identities of the other compounds **7**(**b-d**) were established in a similar ways with all spectroscopic data readily assignable. Further, **7d** was confirmed unambiguously by a single crystal X-ray diffraction (**Fig. 3**).

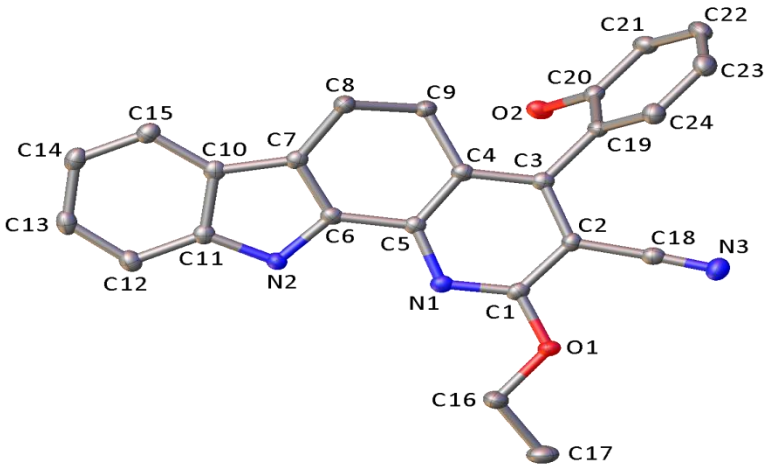
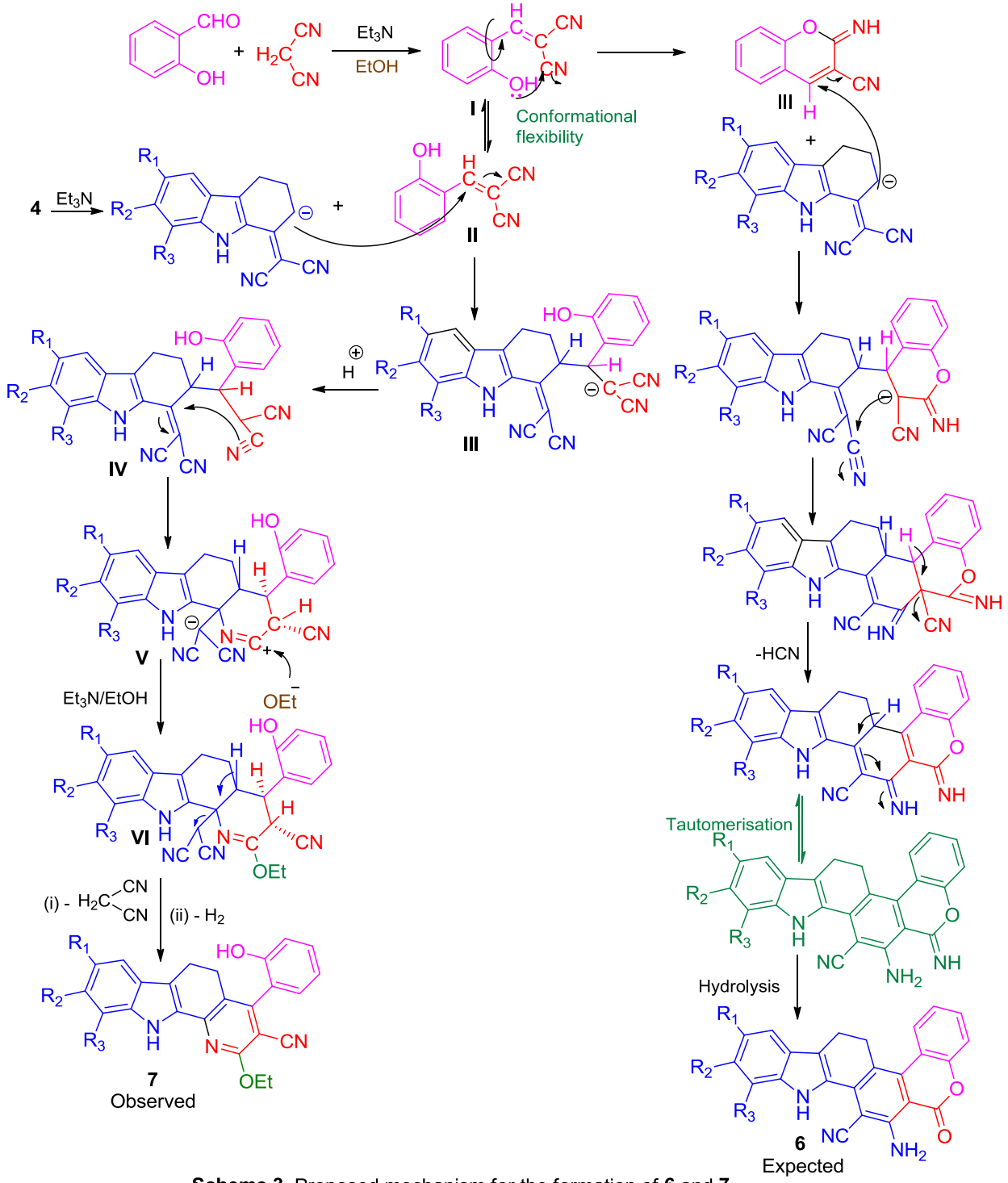


Fig. 3. Structure of **7d** showing the atomic numbering scheme with the thermal ellipsoids depicted at the 50% probability level. Hydrogen atoms are omitted for clarity

A plausible mechanism for the formation of compound **7** (observed) over compound **6** (expected) is depicted in **Scheme 3**. Initially, the salicylaldehyde undergoes Knoevenagel condensation with malononitrile in the presence of base which would give two possible conformers, **I** and **II** (I and II are inter convertible to each other nothing but conformational flexibility in the substrate), which on reaction with **4** affords the respective products **6** (expected) and **7** (observed). The carbanion intermediate from the compound **4** under basic condition on 1,2-Michael addition with the geometrical isomer intermediate **II** derived from intermediate **I** to give the intermediate **III**, which on prototropic shift followed by intramolecular cyclization

affords intermediate **V** through the intermediate **IV**. The nucleophilic attack of ethoxide ion in basic medium to the cyclized intermediate **V** yielded intermediate **VI**. This subsequently loses malononitrile and H_2 furnishing the appropriate product **7**. The reason for the formation of 2-ethoxy-4-(2-hydroxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile **7** over 2-amino-3-imino-3,9,10,15-tetrahydrobenzo[3,4]isochromeno [5,6-*a*]carbazole-1-carbonitrile 6 may be due to the orientation of o-hydroxy phenyl group across the substituted α,α-dicyano olefin.

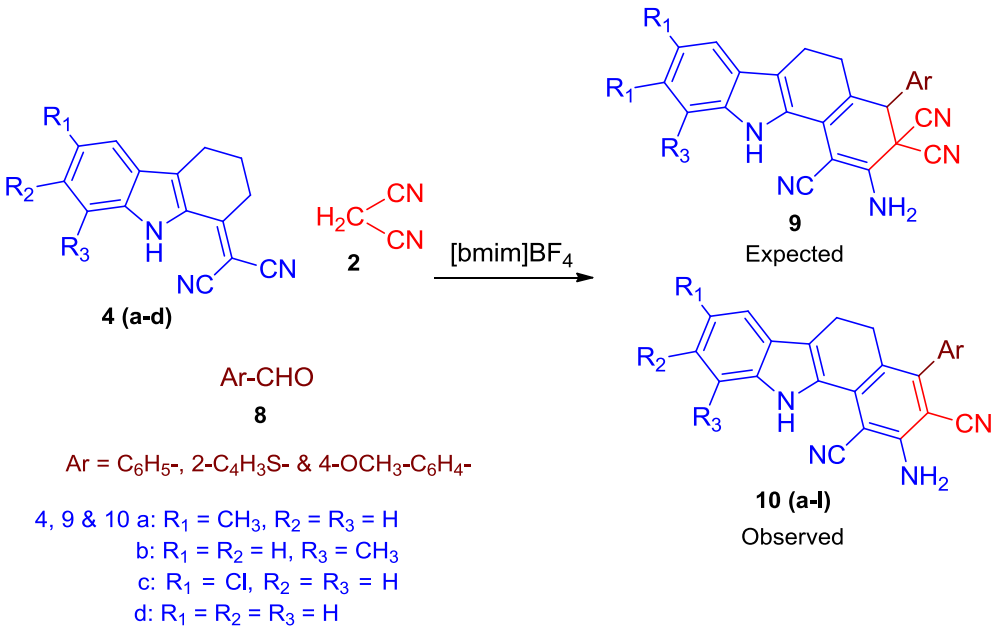


Scheme 3. Proposed mechanism for the formation of **6** and **7**.

Ionic liquids are a new class of solvents entirely composed of ions and they are regarded as substituent for conventional solvents in synthesis due to their non-volatility, non-inflammability, stability and ease of recyclability.[36] In addition, the need for catalyst is avoided

through the use of catalytically active ionic liquids as solvents. Therefore, MCRs in ionic liquids have emerged as a powerful tool in organic chemistry.[37] Based on the above mentioned findings, we report herein for the first time, a highly selective synthesis of benzo[*a*]- annulated carbazoles from dicyanoalkenes in the presence of ionic liquid.

The reaction of **4** with malononitrile **2** and aryl/heteroarylaldehydes **8** upon stirring afforded only one product as indicated by TLC. The structure was established to be 2-amino-4-aryl/heteroaryl-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile **10** rather than 2-amino-4-aryl/heteroaryl-5,6-dihydro-3*H*-benzo[*a*]carbazole-1,3,3-tricarbonitrile **9** based on spectroscopic, X-ray diffraction and elemental analysis data (**Scheme 4**). The reaction condition was optimized and summary of the optimization experiment is provided in **Table 3**.



Scheme 4. Synthesis of 2-amino-4-aryl/hetroaryl-6,5-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile **10**.

Table 3. Optimization of solvent condition **10** (**a-l**)[a]

Entry	Solvent	Reaction condition	Time (h)	Yield (%)[b]
1.	DCM	Rt	10	-
2.	MeOH	Rt	10	-
3.	DMF	Rt	10	-
4.	EtOH	Rt	12	21
5.	[bmim]BF_4	Rt	4	85
6.	[bmim]BF_4	Rt	10	85

[a] Reaction solvent condition: **4 (a-l)** (1.0 mmol), aryl/hetero aldehyde **8** (1.0 mmol), **2** (1.0 mmol), [bmim]BF_4,10 mL, stirred 5 h. [b] Isolated yields

It was found that the reaction could not give the expected product in organic solvents condition (Table 3, entries 1-3). When the reaction can be carried out in medium polar solvent such as EtOH the yield of product was lower than that in ionic liquid (entries 5,6). The above results explored that the polarity of the solvent has played a great role on the reaction process and yield of the product. As revealed in Table 3, [bmim]BF_4 at room temperature for 4 hours appeared to be the best optimized reaction condition.

Based on the appropriate reaction conditions, a series of benzo[*a*]carbazolederivatives were synthesized. The results were summarized in **Table 4.**

Table 4. One-pot synthesis of 2-amino-4-aryl/heteroaryl-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile **10** (**a-l**) in the presence of [bmim]BF_4.

Entry	R_1	R_2	R_3	Ar-	Product	Time (h)	Yield (%)	M.P.(°C)
1.	CH_3	H	H	C_6H_5-	**10a**	4	79	244-246
2.	H	H	CH_3	C_6H_5-	**10b**	4	81	245-247
3.	Cl	H	H	C_6H_5-	**10c**	4.5	70	243-245
4.	H	H	H	C_6H_5-	**10c**	4.5	70	243-245
5.	CH_3	H	H	2-C_4H_3S-	**10e**	4	67	242-244
6.	H	H	CH_3	2-C_4H_3S-	**10f**	4	69	243-245
7.	Cl	H	H	2-C_4H_3S-	**10g**	5	61	241-243
8.	H	H	H	2-C_4H_3S-	**10h**	4	73	240-242
9.	CH_3	H	H	4-OCH_3-C_6H_4-	**10i**	4	75	246-248
10.	H	H	CH_3	4-OCH_3-C_6H_4-	**10j**	4	78	245-247
11.	Cl	H	H	4-OCH_3-C_6H_4-	**10k**	4.5	72	242-244
12.	H	H	H	4-OCH_3-C_6H_4-	**10l**	4	80	243-245

A variety of substrates were submitted to the optimum reaction conditions and the desired products were obtained in excellent yields. This protocol can be applied not only to aromatic aldehydes with electron-donating groups (methoxy group) but also with hetero aromatic aldehyde with excellent yields under the same conditions, which highlighted the wide scope of this condensation.

The structures of the synthesized compounds were consistent with their FT-IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analysis. The FT-IR spectral data of **10a** displayed prominent absorption at 3425cm^{-1} due to NH_2 and indole NH stretchings. The vibration of cyano group was assigned to a strong band at 2209 cm^{-1}. The ^{1}H NMR spectrum of **10a** exhibited a broad singlet for indole NH at δ 9.24 ppm. The three protons at C_{10}, C_7 and C'_4 accounted for multiplets in the region of δ 7.52-7.47 ppm. Two multiplets in the region of δ 7.35-7.33 and δ 7.29-7.28 ppm accounted for C'_6, C'_2, C'_5 and C'_3 protons respectively, a doublet at δ 7.14 ppm (J_o=8.4 Hz) arising due to C_9-H. The amino protons resonated as a singlet at δ 5.14 ppm. The methylene protons of C_6 and C_5 appeared as two multiplets centered at δ 2.81 and δ 2.65 ppm respectively. A sharp singlet at δ 2.43 ppm accounted for three methyl protons at C_8 position. The ^{13}C NMR spectrum displayed 25 resonances in agreement with the proposed structure. The

resonance signals at δ 117.4 and 16.3 were attributed to two cyano and CH_3 carbons. The identities of the other compounds **10** (**b-l**) were established in a similar ways with all spectroscopic data readily assignable. The structure of the compound **10l** was also confirmed by single crystal X-ray diffraction (**Fig. 4**).

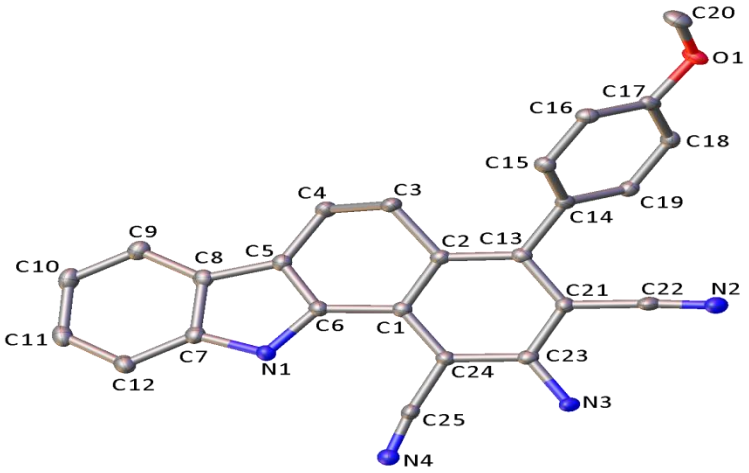
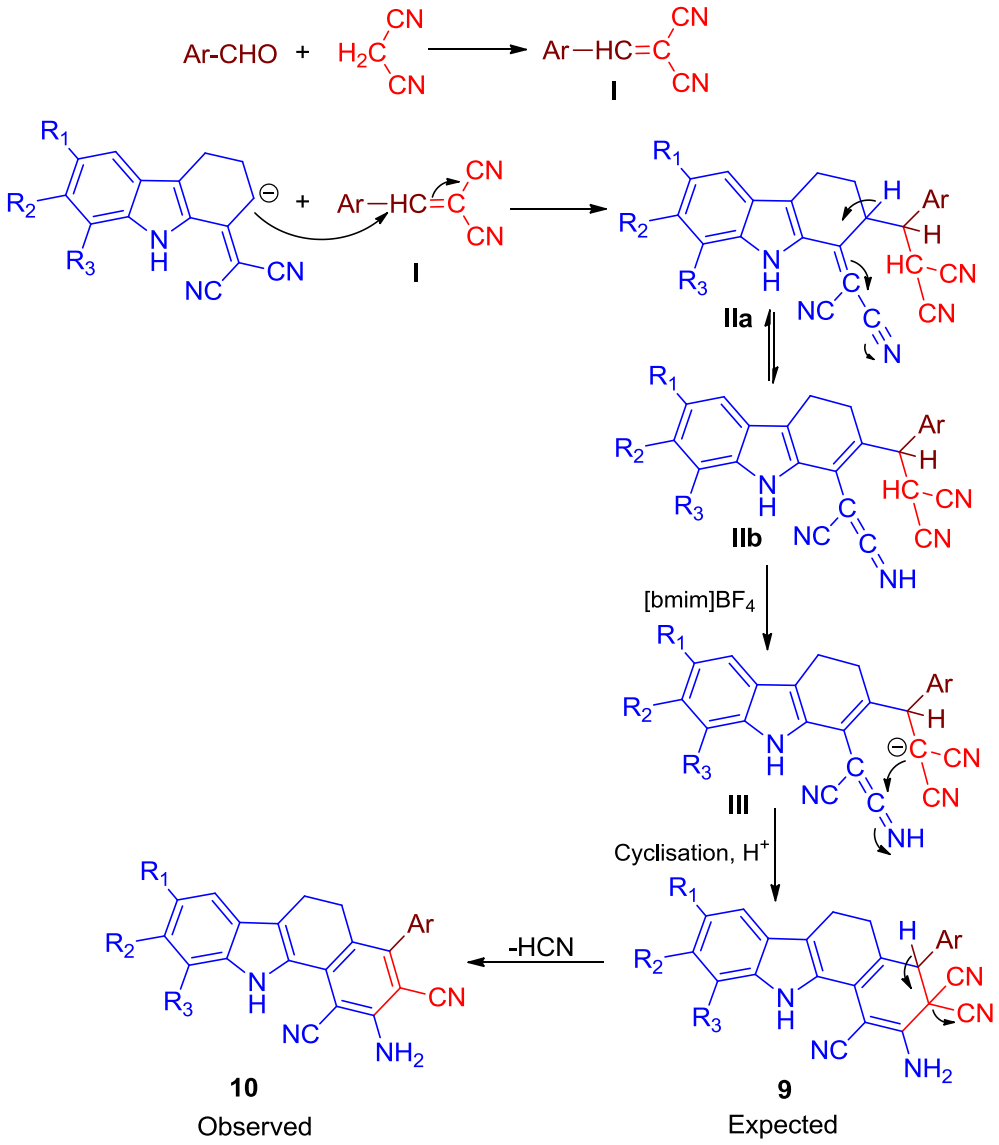


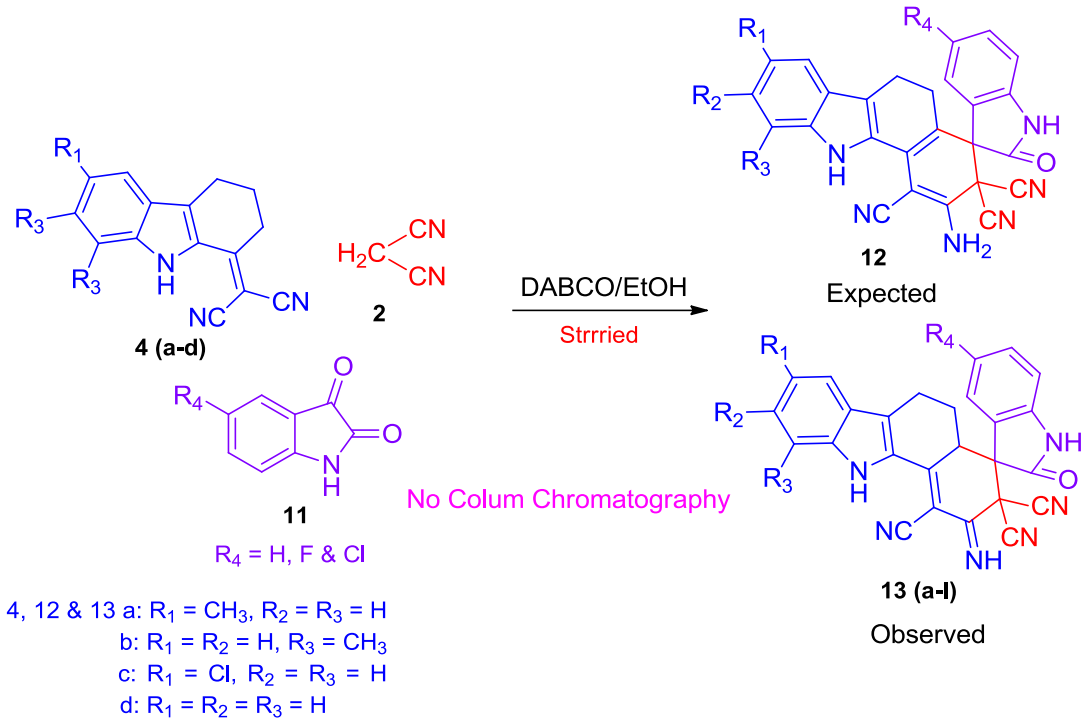
Fig. 4. Structure of **10l** showing the atomic numbering scheme with the thermal ellipsoids depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

A reasonable mechanism for the formation of the product **10** is outlined in **scheme 5**. The first step may proceed via an *in situ* initial formation of the aryl/heteroarylidenemalononitrile **I**, from the Knoevenagel condensation between aryl/heteroaryl aldehyde and malononitrile by loss of water molecule. The second key intermediate **II** Michael adduct (**IIa** stabilizes through its tautomer **IIb**), derived through the carbanion intermediate arises from **4** and the intermediate **I** in presence of ionic liquid [bmim]BF_4 gives the intermediate **III**. Subsequently this intermediate **III** on cyclisation results the formation of the expected product **9**, but the expected product being formed *in situ* on elimination of HCN molecule afforded the observed product **10**. This may be due to the stability of the formation of the aromatized product.



Scheme 5. A plausible mechanism for the formation of **9** and **10**.

In this study we developed a mild and efficient novel protocol for the synthesis of spirooxindole-benzocarbazole derivatives *via* one-pot three component reaction. In a model reaction, a combination of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4,** malononitrile **2** and substituted isatin **11** was chosen to gain synthetic and mechanistic insight into the formation of 2-imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[a]carbazole]-1,3,3-tricarbonitrile **13** derivatives (**Scheme 6**). The expected amino structure **12** was ruled out based on FT-IR, ^{1}H & ^{13}C NMR spectral data and X-ray diffraction. For example, FT-IR spectrum revealed the absence of NH_2 absorption band and the ^{1}H NMR spectrum showed the presence of C_2 imine at δ 10.93 ppm.



Scheme 6. 2-Imino-2'-oxo-5,6-dihydro-11H-spiro[indoline-3',4-benzo[a]carbazole]-1,3,3-tricarbonitrile **13.**

A systematic study was performed to check the effect of different catalysts and solvents and the results are summarized in **Table 5.**

Table 5. Screening of catalyst for the multi-component synthesis of **13a**[a]

Entry	Solvent	Catalyst	Time	Yield (%) [b]
1.	EtOH	Catalyst-free	12	NR
2.	EtOH	K_2CO_3	8	NR
3.	EtOH	Morpholine	8	22
4.	EtOH	Et_3N	8	51
5.	EtOH	Piperidine	7	58
6.	EtOH	DABCO	1	88
7.	EtOH	DABCO	4	88
8.	MeOH	DABCO	4	61
9.	CH_3CN	DABCO	6	49
10.	$CHCl_3$	DABCO	6	54
11.	DMF	DABCO	6	42

[a] **4a**, 1.0 mmol, isatin **11**, (1.0 mmol), catalyst DABCO (0.5 mmol), EtOH 15 mL, stirring 30 min. [b] Isolated yield

To probe the role of catalyst, initially a blank reaction was conducted for the model reaction in ethanol condition, the reaction failed to give the expected product (Table 5, entry 1). At the outset of our studies, reaction was also performed with some commonly available catalysts such as K_2CO_3, morpholine, Et_3N, piperidine and DABCO. It is noteworthy to mention that no product was detected in the presence of K_2CO_3 and much lower yield was furnished by morpholine (entries 2,3). The influence of Et_3N and piperidine in the above reaction was marginal (entries 4,5). Table 5 clearly shows that DABCO is the best catalyst in terms of yield and reaction time (entry 6). To our delight, the desired spirooxindole- benzocarbazole was obtained in 88% yield, and no further improvement was observed when the reaction time increased. Encouraged by these results, we carried out the reaction using various solvents such as EtOH, MeOH, CH_3CN, $CHCl_3$ and DMF (entries 7-11). It was observed that the reaction performed in ethanol gave much better results as compared to other solvents. 1,4-Diazabicyclo[2.2.2]octane (DABCO) has been used as an efficient solid base catalyst and the synthesized compounds were purified without column chromatography. Due to these points this protocol acquired immense interest in the field of organic synthesis.

The structures of compounds **13** (**a-l**) were established on the basis of their elemental analysis and spectral data. The important diagnostic bands in the IR spectrum of **13a** were assigned. The stretching vibrations at 3452, 3383 and 3279 cm^{-1} corresponding to indole NH, oxindole NH and imino NH respectively. The cyano group stretching vibration was assigned to a strong band at 2219 cm^{-1} The ^1H NMR spectrum displayed three broad singlets at δ 11.58, δ 11.36 andδ 10.93 ppm owing to two indole NH and imino NH protons respectively. The signal due to C_{10}-H was visible as a doublet at δ 7.53 (J_o = 8.0 Hz), and the proton at C'_6 resonated as multiplets in the region of δ 7.41-7.37 ppm. A sharp singlet at δ 7.35 ppm was due to C_7-H, the aromatic protons at C'_7 and C'_4 positions appeared as doublets at δ 7.22 and δ 7.06 ppm (J_o = 7.6 Hz & J_o = 7.6 Hz) respectively. The C_5'-H proton was visible as a triplet at δ 7.02 (J_o = 7.6 Hz), a singlet at δ 6.96 ppm (J_o = 8.0 Hz) due to C_9-H proton. A remarkable doublet of doublets at δ 3.70 (J_{cis} = 3.2 Hz and J_{trans} = 12.0 Hz) was due to heteroannular proton. The aliphatic protons at C_6 resonated as multiplets in the region of 2.98-2.95 ppm. A sharp singlet at δ 2.34 ppm accounted for the three methyl protons at C_8 position, the methylene protons of C_{5b} and C_{5a} appeared as two multiplets centered at δ 1.67 and δ 1.30 ppm respectively.

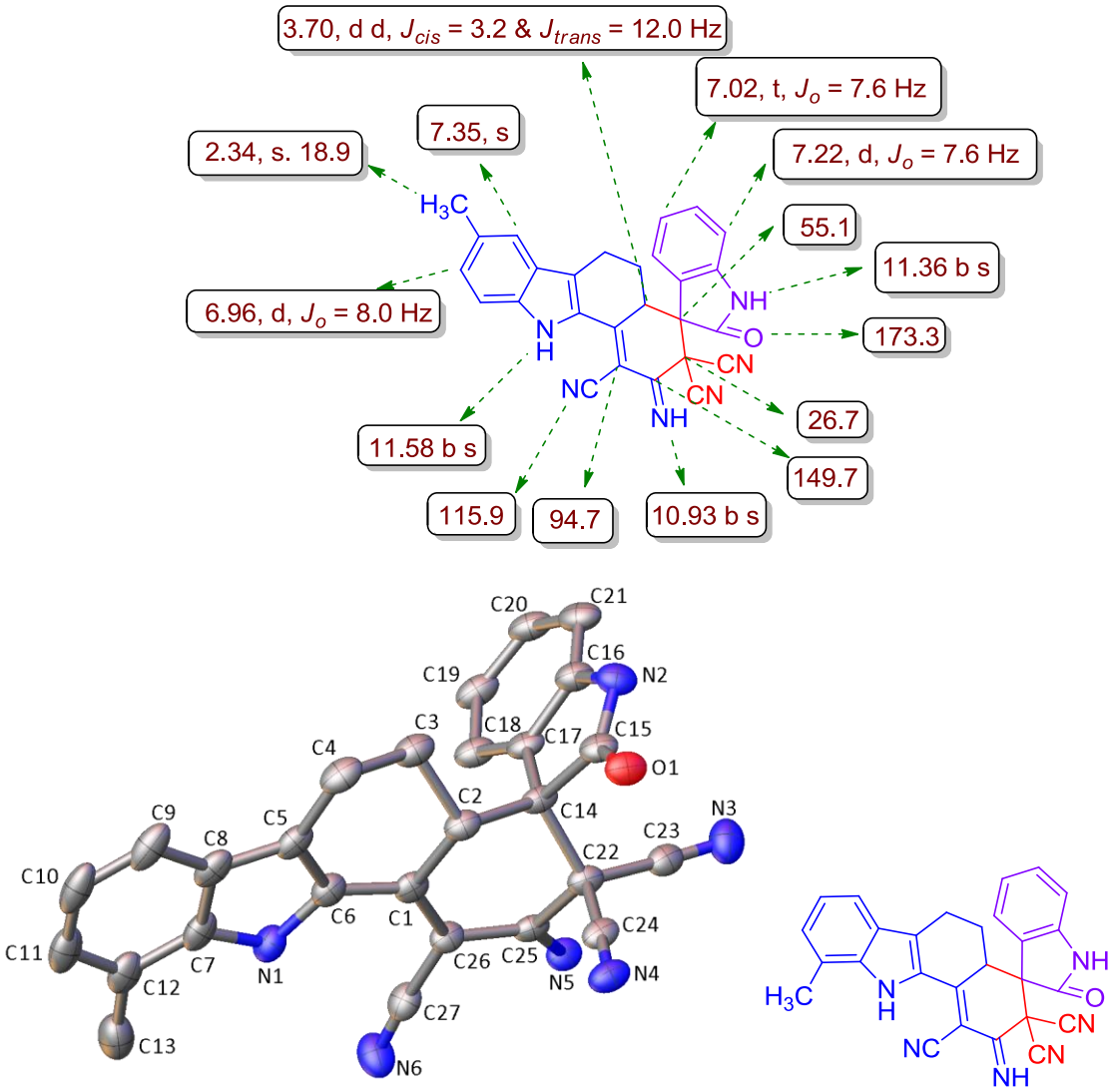


Fig. 5. Structure of **13b** showing the atomic numbering scheme with the thermal ellipsoids depicted at the 50% probability level. Hydrogen atoms and disordered water molecules are omitted for clarity.

With optimized reaction conditions in hand, to delineate this approach, particularly in regard to library construction, this methodology was evaluated by using a variety of isatin derivatives **Fig. 6** and **Table 6**.

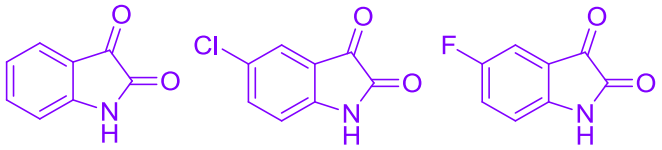
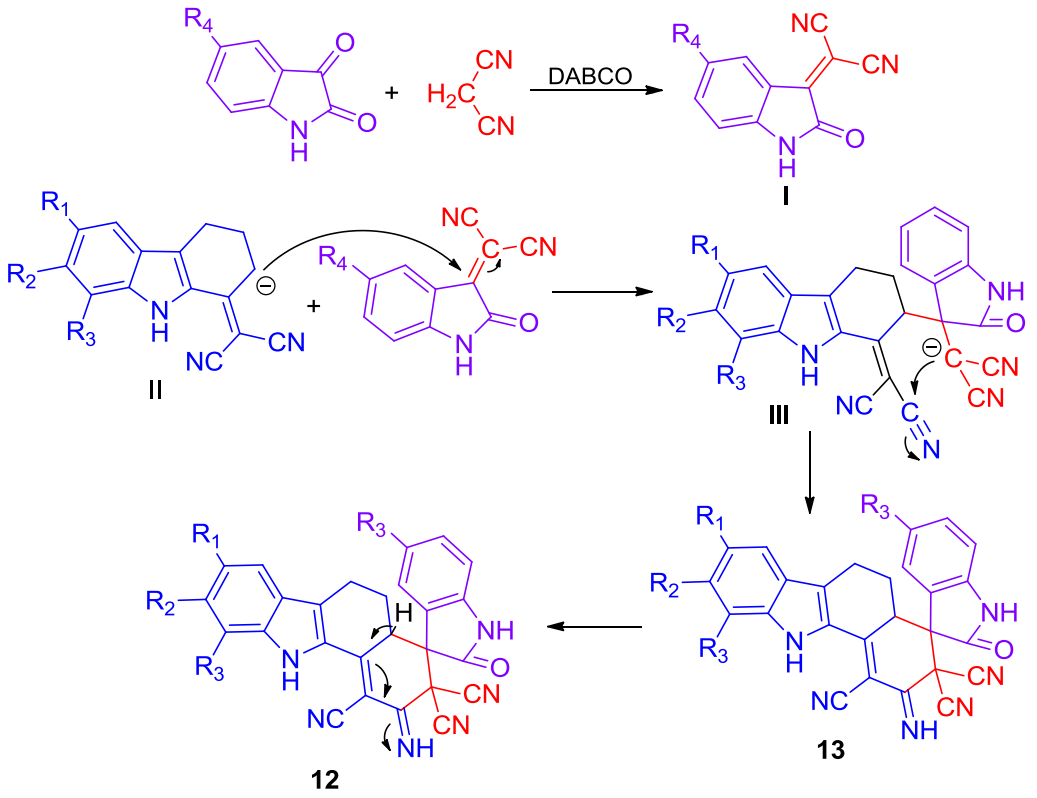


Fig. 6. Diversity of isatine

Table 6. One-pot synthesis of 2-imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **13** (**a-l**) catalyzed by DABCO

Entry	R_1	R_2	R_3	R_4	Product	Time (h)	Yield (%)	M.P.(°C)
1.	CH_3	H	H	H	**13a**	1	83	222-224
2.	H	H	CH_3	H	**13b**	1	81	223-225
3.	Cl	H	H	H	**13c**	1.5	79	225-257
4.	H	H	H	H	**13d**	1	80	223-225
5.	CH_3	H	H	F	**13e**	1.5	74	224-226
6.	H	H	CH_3	F	**13f**	1.5	76	225-227
7.	Cl	H	H	F	**13g**	2	71	220-222
8.	H	H	H	F	**13h**	1.5	80	223-225
9.	CH_3	H	H	Cl	**13i**	1	86	220-222
10.	H	H	CH_3	Cl	**13j**	1	83	221-223
11.	Cl	H	H	Cl	**13k**	1	90	219-221
12.	H	H	H	Cl	**13l**	1	85	223-225

To explain the mechanism of this multicomponent reaction, we propose the following reaction course (**scheme 7**). DABCO-assisted Knoevenagel condensation of the isatin with malononitrile yields 2-(2-oxoindolin-3-ylidene)malononitrile **I**. The 1,4-Michael addition of the carbanion intermediate **II** derived from the synthon, 1-(α,α-dicyano methylene)-2,3,4,9-tetrahydrocarbazole to Knoevenagel adduct provides the intermediate **III**, which on intramolecular cyclization to afford the final imino product **13**.



Scheme 7. Possible mechanism for the formation of **12** and **13**

Conclusion

1-(α,α-Dicyanomethylene)-2,3,4,9-tetrahydrocarbazole and malononitrile were found to be good reactants for the synthesis of aryl- and heteroaryl-annulated carbazoles *via* one-pot MCRs with salicylaldehyde, aryl/heteroaryl aldehydes and isatin which afforded of novel highly substituted pyrido[2,3-*a*]carbazoles, benzo[*a*]carbazoles and spirooxindoles-benzocarbazole in good to excellent yield. On the whole, the works presented here are significant in terms of yield, reaction time, cost effectiveness, eco-friendliness and wide scope to obtain diversity of the products and potentially bioactive compounds in very good to excellent yields.

Experimental section

General: All the chemicals were bought from Sigma-Aldrich and Merckand were utilized for the process without further purification. Melting points (m.p.) were determined on a Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and are uncorrected. They are expressed in degree centigrade (°C). FT-IR spectra were recorded on Avatar Model FT-IR (4000–400 cm^{-1})

spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Agilent- 400 MHz (^{1}H) and 100 MHz (^{13}C) spectrometers respectively in $CDCl_3$ using TMS (tetramethylsilane) as internal reference; chemical shifts are expressed in parts per million (ppm); coupling constants (*J*) are reported in hertz (Hz) and the terms J_o and J_m refer to ortho coupling constant and meta coupling constant. The signals were characterized as s (singlet), d (doublet), t (triplet), m (multipiet), bs (broad singlet) and dd (doublet, and doublet). Microanalyses were carried out using Vario EL III model CHNS analyzer (Vario, Germany). When known compounds had to be prepared according to literature procedures and pertinent references are given. The purity of the products was tested by TLC plates coated with silica gel-G using petroleum ether and ethyl acetate in the ratio of 1:1 as developing solvents.

General procedure for the preparation of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole 4

A mixture of 2,3,4,9-tetrahydro-1*H*-carbazole-1-one **1** (1.0 mmol), malononitrile **2** (1.0 mmol), ammonium acetate **3** (1.2 mmol) and four drops of acetic acid in 10.0 mL of toluene was refluxed at 120 °C for 6 h. On cooling, the precipitate that formed was filtered off, washed with petroleum ether and dried. The crude product thus obtained was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (99:1) to yield the corresponding product 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4**.

1-(Dicyanomethylene)-6-methyl-2,3,4,9-tetrahydrocarbazole (4a): Pale yellow solid; yield: 172 mg (70%); m.p. 199-201°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3381 (NH), 2211(CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.25 (b s, 1H, N_9-H), 7.38 (s, 1H, C_5-H), 7.30-7.25 (m, 2H, C_8 & C_7-H), 2.99-2.95 (m, 4H, C_4 & C_3-2H), 2.43 (s, 3H, C_6-CH_3), 2.12-2.07 (m, 2H, C_2-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 160.2 (C_1), 138.0 (C_{9a}), 131.2 (C_{8a}), 130.9 (C_6), 130.3 (C_{4b}), 128.5 (C_7), 125.6 (C_5), 120.2 (C_{4a}), 116.5 (C_8), 113.6 (CN & CN), 112.0 (C_1'), 31.4 (C_2), 23.4 (C_4), 21.9 (C_3), 21.3 (CH_3); Anal. calcd. for: $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.80; H, 5.26; N, 16.92 %.

1-(Dicyanomethylene)-8-methyl-2,3,4,9-tetrahydrocarbazole (4b): Pale yellow solid; yield: 160 mg (65%); m.p. 197-199 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3385 (NH), 2209 (CN); ^{1}H NMR (400

MHz, $CDCl_3$) (ppm) δ_H: 9.32 (b s, 1H, N_9-H), 7.46 (d, 1H, C_5-H, J_o = 7.8 Hz), 7.24-7.20 (m, 1H, C_7-H), 7.09 (t, 1H, C_7-H, J_o = 7.8 Hz), 3.02-2.96 (m, 4H, C_4 & C_3-2H), 2.47 (s, 3H, C_{10}-CH_3), 2.13-2.07(m, 2H, C_2-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 160.7 (C_1), 138.3 (C_{9a}), 131.0 (C_{8a}), 130.5 (C_6), 130.7 (C_{4b}), 128.9 (C_7), 125.2 (C_5), 121.0 (C_{4a}), 116.7 (C_8), 113.8 (CN & CN), 112.4 (C_1'), 31.6 (C_2), 23.5 (C_4), 21.6 (C_3), 21.5 (CH_3); Anal. calcd. for: $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.62; H, 5.34; N, 16.93 %.

1-(Dicyanomethylene)-6-chloro-2,3,4,9-tetrahydrocarbazole (4c): Pale yellow solid; yield: 149 mg (56%); m.p. 198-200 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3363 (NH), 2205 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.36 (b s, 1H, N_9-H), 7.59 (s, 1H, C_5-H), 7.36-7.34 (m, 2H, C_8 & C_7-H), 3.01-2.95 (m, 4H, C_4 & C_3-2H), 2.14-2.07 (m, 2H, C_2-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 160.3 (C_1), 138.3 (C_{9a}), 131.3 (C_{8a}), 131.0 (C_6), 130.5 (C_{4b}), 128.7 (C_7), 125.4 (C_5), 120.3 (C_{4a}), 116.4 (C_8), 113.7 (CN & CN), 112.2 (C_1'), 31.3 (C_2), 23.5 (C_4), 21.7 (C_3); Anal. calcd. for: $C_{15}H_{10}ClN_3$: C, 67.30; H, 3.77; N, 15.70. Found: C, 67.39; H, 3.72; N, 15.77 %.

1-(Dicyanomethylene)-2,3,4,9-tetrahydrocarbazole (4d): Pale Yellow solid; yield: 170 mg (73%); m.p. 196-197 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3366 (NH), 2216 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 10.8 (b s, 1H, N_9-H), 7.69-7.63 (m, 2H, C_8 & C_5-H), 7.41-7.37 (t, 1H, C_6-H), 7.15-7.11 (t, 1H, C_7-H), 2.96-2.94 (m, 4H, C_4 & C_3-2H), 2.00 (m, 2H, C_2-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 161.0 (C_1), 140.5 (C_{9a}), 130.6 (C_{8a}), 128.4 (C_{4b}), 128.1 (C_7), 125.2 (C_6), 120.9 (C_5), 120.7 (C_{4a}), 114.9 (CN), 114.5 (CN), 113.7 (C_8), 69.5 (C_1'), 31.2 (C_2), 23.1 (C_4), 21.2 (C_3); Anal. calcd. for: $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.31; H, 4.71; N, 18.10 %.

General procedure for the preparation of pyrido[2,3-a]carbazole 7

The solution of salicylaldehyde **5** (1.0 mmol), 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (1.0 mmol), malononitrile **2** (1.0 mmol) and trace amount of triethylamine (0.2 mL) in 15.0 mL of ethanol was heated under reflux for 2 h and the progress of the reaction was monitored by TLC. After completion of reaction the crude was poured into ice-water, the solid that separated out was filtered washed with water and purified over column chromatography using petroleum ether: ethyl acetate (95:5) as eluent to afford the pure product.

2-Ethoxy-4-(2-hydroxyphenyl)-8-methyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (7a): Yellow solid; yield: 328 mg (83%); m.p. 259-261 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3379 (OH), 3211 (NH), 2228 (CN), 1555 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 10.22 (b s, 1H, C_2'-OH), 9.26 (b s, 1H, N_{11}-H), 7.27 (d, 1H, C_{10}-H, J_o = 7.6 Hz), 7.18-7.16 (m, 2H, C_7 & C_6'-H), 7.02 (d d, 1H, C_9-H, J_m = 1.6 & J_o = 7.6 Hz), 6.95-6.92 (m, 2H, C_5' & C_3'-H), 6.86-6.82 (m, 1H, C_4'-H), 4.60 (q, 2H, C_2-OC**H**$_2$CH$_3$, J = 7.2 Hz), 2.82-2.60 (m, 4H, C_6 & C_5-2H), 2.23 (s, 3H, C_8-CH_3), 1.39 (t, 3H, C_2-OCH$_2$C**H**$_3$, J = 7.2 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.1 (C_2), 154.2 (C_{11b}), 151.7 (C'$_2$), 148.7 (C_4), 136.8 (C_{10a}), 132.6 (C_{11a}), 130.2 (C'$_6$), 129.7 (C_4'), 128.6 (C'$_1$), 126.7 (C_8), 125.8 (C_{6b}), 122.8 (C_{4a}), 122.7 (C_5'), 119.3 (C_9), 119.0 (C_7), 117.8 (C_3'), 116.2 (C_{6a}), 116.1 (CN), 111.8 (C_{10}), 93.2 (C_3), 62.6 (O**C**H$_2$CH$_3$), 25.0 (C_5), 21.4 (C_6), 19.3 (CH_3), 14.7 (OCH$_2$**C**H$_3$); Anal. calcd. for: $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.84; H, 5.39; N, 10.55 %.

2-Ethoxy-4-(2-hydroxyphenyl)-10-methyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (7b): Yellow solid; yield: 312 mg (79%); m.p. 260-262 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3345 (OH), 3283 (NH), 2223 (CN), 1552 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.47 (s, 1H, C_2'-OH), 9.24 (b s, 1H, N_{11}-H), 7.28 (d, 1H, C_7-H, J_o = 7.2 Hz), 7.21-7.16 (m, 1H, C_8-H), 7.03 (dd, 1H, C_6'-H, J_m = 1.6 & J_o = 7.6 Hz), 6.96-6.88 (m, 3H, C_9, C_5' & C_3'-H), 6.85 (t, 1H, C_4'-H), 4.57 (q, 2H, C_2-OC**H**$_2$CH$_3$, J = 7.6 Hz), 2.82-2.68 (m, 4H, C_6 & C_5-2H), 2.50 (s, 3H, C_{10}-CH_3), 1.40 (t, 3H, C_2-OCH$_2$C**H**$_3$, J = 7.6 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.3 (C_2), 154.5 (C_{11b}), 151.6 (C'$_2$), 148.4 (C_4), 136.7 (C_{10a}), 132.5 (C_{11a}), 130.4 (C'$_6$), 129.5 (C_4'), 128.4 (C'$_1$), 126.9 (C_8), 125.7 (C_{6b}), 122.9 (C_{4a}), 122.6 (C_5'), 119.4 (C_9), 119.2 (C_7), 117.9 (C_3'), 116.4 (C_{6a}), 116.3 (CN), 111.9 (C_{10}), 93.3 (C_3), 62.7 (O**C**H$_2$CH$_3$), 25.1 (C_5), 21.3 (C_6), 18.3 (CH_3), 15.4 (OCH$_2$**C**H$_3$); Anal. calcd. for: $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.99; H, 5.28; N, 10.70 %.

2-Ethoxy-4-(2-hydroxyphenyl)-8-chloro-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (7c): Yellow solid; yield: 302 mg (73%); m.p. 263-265 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3352 (OH), 3189 (NH), 2231 (CN), 1553 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.79 (s, 1H, C_2'-OH), 8.63 (b s, 1H, N_{11}-H), 7.70 (d, 1H, C_{10}-H, J_o= 7.6 Hz), 7.66-7.63 (m, 3H, C_9, C_7 & C_6'-H), 7.43-7.34 (m, 3H, C_5', C_4 '& C_3'-H), 4.82 (q, 2H, C_2-OCH$_2$C**H**$_3$, J = 7.0 Hz), 2.92-2.81

(m, 4H, C_6 & C_5-2H), 1.50 (t, 3H, C_2-$OCH_2C\mathbf{H}_3$, *J* = 7.0 Hz); Anal. calcd. for: $C_{24}H_{18}ClN_3O_2$: C, 69.31; H, 4.36; N, 10.10. Found: C, 69.42; H, 4.30; N, 10.3 %.

2-Ethoxy-4-(2-hydroxyphenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (7d): Yellow solid; yield: 304 mg (80%); m.p. 258-260 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3378 (OH), 3219 (NH) 2223 (CN), 1553 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 10.22 (s, 1H, C_2'-OH), 9.57 (b s, 1H, N_{11}-H), 7.37 (d, 1H, C_7-H, J_o = 7.6 Hz), 7.30 (d, 1H, C_6'-H, J_o = 8.4 Hz), 7.12 (t, 1H, C_8-H, *J* = 7.6 Hz), 7.08-7.04 (m, 1H, C_{10}-H), 6.97-6.86 (m, 3H, C_5', C_4' & C_3'-H), 6.79 (t, 1H, C_9-H, J_o = 7.6 Hz), 4.48 (q, 2H, C_2-$OC\mathbf{H}_2CH_3$, *J* = 7.0 Hz), 2.78-2.70 (m, 4H, C_6 & C_5-2H), 1.33 (t, 3H, C_2-$OCH_2C\mathbf{H}_3$, *J* = 7.0 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.1 (C_2), 154.0 (C_{11b}), 151.7 (C'$_2$), 148.3 (C_4), 138.0 (C_{10a}), 132.4 (C_{11a}), 130.2 (C_6'), 129.6 (C_4'), 126.5 (C_1'), 123.9 (C_{6b}), 122.7 (C_{4a}), 122.6 (C'$_5$), 119.6 (C_9), 119.5 (C8), 119.3 (C_7), 118.3 (C_3'), 116.2 (C_{6a}), 116.0 (CN), 111.8 (C_{10}), 93.5 (C_3), 62.6 ($O\mathbf{C}H_2CH_3$), 24.9 (C_5), 19.2 (C_6), 14.5 ($OCH_2\mathbf{C}H_3$); Anal. calcd. for: $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 75.48; H, 5.08; N, 11.09 %.

Synthrsis of benzo[a]carbazole 10

A dry 50 mL round bottom flask was charged with 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (1.0 mmol), aryl/hetero aldehyde **8** (1.0 mmol), malononitrile **2** (1.0 mmol) and the ionic liquid ([bmim]BF_4, 10.0 mL). The reaction mixture was stirred for 5 h. After completion of the reaction as indicated by TLC, the reaction mixture was add quenched water (30.0 mL), and extracted with ethyl acetate (3 x 30 mL). The organic layer was washed with water, and then dried over anhydrous Na_2SO_4. The crude residue was purified by column chromatography over silica gel, eluting with petroleum ether: ethyl acetate (93:7) to afford the corresponding pure product 2-amino-4-aryl/hetroaryl-6,5-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile.

2-Amino-8-methyl-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10a): Yellow solid; yield: 295 mg (79%); m.p. 244-246 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3425 (NH_2 & NH), 2209 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.24 (b s, 1H, N_{11}-H), 7.52-7.47 (m, 3H, C_{10}, C_7 & C_4'-H), 7.35-7.33 (m, 2H, C_6' & C_2'-H), 7.29-7.28 (m, 2H, C_5' & C_3'-H), 7.14 (d, 1H, C_9-H, J_o = 8.4 Hz), 5.14 (s, 2H, C_2-NH_2), 2.83-2.79 (m, 2H, C_6-2H), 2.67-2.63 (m, 2H, C_5-2H) 2.43 (s, 3H, C_8-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 150.9 (C_2), 137.5 (C_4), 137.3

(C_{11b}), 136.2 (C_{10a}), 129.0 (C_1'), 128.9 (C_5' & C_3'), 128.7 (C_{4a}), 128.4 (C_6' & C_2'),125.6 (C_4'), 125.0 (C_{6b}), 124.6 (C_{10a}), 121.1(C_8), 121.1 (C_{10}), 120.8 (C_9 & C_7), 118.3 (C_{6a}), 117.4 (C_1-CN & C_3-CN), 115.9 (C_1 & C_3), 26.1 (C_5), 19.6 (C_6), 16.3 (CH_3); Anal. calcd. for: $C_{25}H_{18}N_4$: C, 80.19; H, 4.85; N, 14.96. Found: C, 80.28; H, 4.79; N, 14.89 %.

2-Amino-10-methyl-4-phenyl-5,6-dihydro-11*H*-benzo[a]carbazole-1,3-dicarbonitrile (10b): Yellow solid; yield: 302 mg (81%); m.p. 245-247 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3466 (asymm NH_2), 3373 (symm NH_2 and indole NH) 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.31 (b s, 1H, N_{11}-H), 7.53-7.47 (m, 3H, C_9, C_8 & C_4'-H), 7.41 (d, 1H, C_7-H, J_o = 7.2 Hz), 7.31-7.28 (m, 2H, C_6' & C_2'-H), 7.12-7.05 (m, 2H, C_5' & C_3'-H), 5.15 (s, 2H, C_2-NH_2), 2.85-2.81 (m, 2H, C_6-2H), 2.69-2.65 (m, 2H, C_5-2H), 2.56 (s, 3H, C_{10}-CH_3); Anal. calcd. for: $C_{25}H_{18}N_4$: C, 80.19; H, 4.85; N, 14.96. Found: C, 80.10; H, 4.79; N, 14.87 %.

2-Amino-8-chloro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10c): Yellow solid; yield: 275 mg (70%); m.p. 243-245 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3410 (asymm NH_2), 3389 (symm NH_2) 3309 (indole NH), 2214 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.35 (b s, 1H, N_{11}-H), 7.53-7.48 (m, 4H, C_7, C_6', C_4' & C_2'-H), 7.38 (d, 1H, C_{10}-H, J_o = 8.8 Hz), 7.29-7.23 (m, 3H, C_9, C_5' & C_3'-H), 5.16 (s, 2H, C_2-NH_2), 2.81-2.78 (m, 2H, C_6-2H), 2.69-2.65 (m, 2H, C_5-2H); Anal. calcd. for: $C_{24}H_{15}ClN_4$: C, 73.00; H, 3.83; N, 14.19. Found: C, 73.09; H, 3.88; N, 14.11 %.

2-Amino-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10d): Yellow solid; yield: 273 mg (76%); m.p. 246-248 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3456 (asymm NH_2), 3396 (symm NH_2), 3363 (indol NH), 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.33 (b s, 1H, N_{11}-H), 7.57 (d, 1H, C_7-H, J_o = 8.4 Hz), 7.53-7.45 (m, 4H, C_{10}, C_8, C_6'& C_2'-H), 7.33-7.28 (m, 3H, C_9, C_5' & C_3'-H), 7.25-7.13 (m, 1H, C_4'-H), 5.15 (s, 2H, C_2-NH_2), 2.86-2.82 (m, 2H, C_6-2H), 2.69-2.65 (m, 2H, C_5-2H); Anal. calcd. for: $C_{24}H_{16}N_4$: C, 79.98; H, 4.47; N, 15.55. Found: C, 79.89; H, 4.51; N, 15.48 %.

2-Amino-8-methyl-4-(thiophen-2-yl)-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10e):Yellow solid; yield: 254 mg (67%); m.p. 242-244 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3414 (asym

NH_2), 3352 (symm NH_2 & indole NH), 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.21 (b s, 1H, N_{11}-H), 7.52 (d, 1H, C_{10}-1H, J_o = 5.2 Hz), 7.35-7.33 (m, 2H, C_7 & C_3'-H) 7.18-7.10 (m, 3H, C_9, C_4 '& C_2'-H), 5.13 (s, 2H, C_2-NH_2), 2.85-2.79 (m, 4H, C_6-2H); Anal. calcd. for: $C_{23}H_{16}N_4S$: C, 72.61; H, 4.24; N, 14.73. Found: C, 72.58; H, 4.28; N, 14.63 %.

2-Amino-10-methyl-4-(thiophen-2-yl)-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10f): Yellow solid; yield: 248 mg (69%); m.p. 243-245 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3460 (asym NH_2), 3342 (symm NH_2 & NH), 2214 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.28 (b s, 1H, N_{11}-H), 7.53-7.51 (m, 1H, C_8-H), 7.42 (d, 1H, C_7-H, J_o = 7.6 Hz), 7.18-7.15 (m, 1H, C_3'-H), 7.12-7.06 (m, 3H, C_9, C_4' & C_2'-H), 5.15 (s, 2H, C_2-NH_2), 2.90-2.86 (m, 2H, C_6-2H), 2.83-2.79 (m, 2H, C_5-2H) 2.55 (s, 3H, C_{10}-CH_3); Anal. calcd. for: $C_{23}H_{16}N_4S$: C, 72.61; H, 4.24; N, 14.73. Found: C, 72.70; H, 4.19; N, 14.65 %.

2-Amino-8-chloro-4-(thiophen-2-yl)-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10g): Yellow solid; yield: 244 mg (61%); m.p. 241-243 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3404 (asym NH_2), 3350 (symm NH_2 & NH), 2215 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.33 (b s, 1H, N_{11}-H), 7.53-7.36 (m, 3H, C_{10}, C_7 & C_3'-1H) 7.25-7.17 (m, 3H, C_9, C_4' & C_2'-H), 5.16 (s, 2H, C_2-NH_2), 2.83-2.81 (m, 4H, C_6 & C_5-2H), 2.44 (s, 3H, C_8-CH_3); Anal. calcd. for: $C_{22}H_{13}ClN_4S$: C, 65.91; H, 3.27; N, 13.98. Found: C, 65.82; H, 3.32; N, 13.90 %.

2-Amino-4-(thiophen-2-yl)-5,6-dihydro-11H-benzo[a]carbazole-1,3-dicarbonitrile (10h): Yellow solid; yield: 262 mg (73%); m.p. 240-242 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3477 (asym NH_2), 3398 (symm NH_2) 3352 (indol NH), 2211 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.30 (b s, 1H, N_{11}-H), 7.57 (d, 1H, C_7-H, J_o = 8.0 Hz), 7.53 (d, 1H, C_2'-H, J_o= 6.2 Hz), 7.46 (d, 1H, C_{10}-H, J_o = 8.0 Hz), 7.31 (t, 1H, C_8-H, J_o = 8.0 Hz), 7.18-7.11 (m, 3H, C_9, C_4' & C_3'-H), 5.15 (s, 2H, C_2-NH_2), 2.90-2.86 (m, 2H, C_6-2H), 2.83-2.79 (m, 2H, C_5-2H); Anal. calcd. for: $C_{22}H_{14}N_4S$: C, 72.11; H, 3.85; N, 15.29; S, 8.75. Found: C, 72.21; H, 3.79; N, 15.35 %.

2-Amino-8-methyl-4-(4-methoxyphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10i): Yellow solid; yield: 303 mg (75%); m.p. 246-248 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3406 (NH_2 & NH), 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.23 (b s, 1H, N_{11}-

H), 7.35-7.33 (m, 2H, C_{10} & C_7-H), 7.25 (m, 2H, C_6' & C_2'-H), 7.13 (d, 1H, C_9-H, J_o = 8.4 Hz), 7.04-7.01 (m, 2H, C_5' & C_3'-H), 5.12 (s, 2H, C_2-NH_2), 3.87 (s, 3H, C_4'-OCH_3), 2.82-2.79 (m, 2H, C_6-2H), 2.70-2.66 (m, 2H, C_5-2H), 2.44 (s, 3H, C_{10}-CH_3); Anal. calcd. for: $C_{26}H_{20}N_4O$: C, 77.21; H, 4.98; N, 13.85. Found: C, 77.12; H, 4.94; N, 13.83 %.

2-Amino-10-methyl-4-(4'-methoxyphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10j): Yellow solid; yield: 315 mg (78%); m.p. 245-247 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3435 (asymm NH_2), 3385 (symm NH_2 & indole NH), 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.30 (b s, 1H, N_{11}-H), 7.42 (d, 1H, C_7-H, J_o = 8.0 Hz), 7.24-7.22 (m, 2H, C_9 & C_8-H), 7.10-7.07 (m, 2H, C_6' & C_2'-H), 7.03-7.01 (m, 2H, C_5' & C_3'-H), 5.13 (s, 2H, C_2-NH_2), 3.87 (s, 3H, C_4'-OCH_3), 2.85-2.82 (m, 2H, C_6-2H), 2.72-2.67 (m, 2H, C_5-2H), 2.56 (s, 3H, C_{10}-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C:160.0 (C'$_4$), 150.9 (C_2), 148.5 (C_4), 137.5 (C_{11b}), 136.1(C_{10a}), 129.8 (C_6' & C_2'), 129.4 (C_{4a}), 129.1 (C_{6b}), 125.6 (C_1'), 125.0 (C_{10a}), 124.9 (C_8), 121.1 (C_{10}), 120.9 (C_9), 120.8 (C_7), 118.4 (C_{6a}), 117.3 (C_1-CN & C_3-CN), 116.1 (C_5' & C_3'), 114.2 (C_1 & C_3), 55.2 (OCH_3), 26.1 (C_5), 19.7 (C_6), 16.3 (CH_3); Anal. calcd. for: $C_{26}H_{20}N_4O$: C, 77.21; H, 4.98; N, 13.85. Found: C, 77.31; H, 4.93; N, 13.78 %.

2-Amino-8-chloro-4-(4'-methoxyphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazole-1,3-dicarbonitrile (10k): Yellow solid; yield: 306 mg (72%); m.p. 242-244 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3406 (NH_2 & NH), 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.35 (b s, 1H, N_{11}-H), 7.52 (d, 1H, C_7-H, J_m = 1.6 Hz), 7.38 (d, 1H, C_{10}-H, J_o = 8.8 Hz), 7.23-7.20 (m, 3H, C_7, C_6' & C_2'-H), 7.04-7.01 (m, 2H, C_5' & C_3'-H), 5.14 (s, 2H, C_2-NH_2), 3.87 (s, 3H, C_4'-OCH_3), 2.82-2.77 (m, 2H, C_6-2H), 2.72-2.68 (m, 2H, C_5-2H); Anal. calcd. for: $C_{25}H_{17}ClN_4O$: C, 70.67; H, 4.03; N, 13.19. Found: C, 70.76; H, 4.08; N, 13.13%.

2-Amino-4-(4-methoxyphenyl)-5,6-dihydro-11H-benzo[*a*]carbazole-1,3-dicarbonitrile (10l): Yellow solid; yield: 312 mg 80 %; m.p. 243-245 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3377 (aymm NH_2), 3337 (symm NH_2), 3233 (NH), 2210 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.32 (b s, 1H, N_{11}-H), 7.57 (d, 1H, C_7-H, J_o = 7.6 Hz), 7.46 (d, 1H, C_{10}-H, J = 7.6 Hz), 7.30 (t, 1H, C_8-H, J_o = 7.6 Hz), 7.25-7.21 (m, 2H, C_6' & C_2'-H), 7.15 (t, 1H, C_9-H, J_o = 7.6 Hz), 7.03-7.01 (m, 2H,

C_5' & C_3'-H), 5.13 (s, 2H, C_2-NH_2), 3.87 (s, 3H, C_4'-OCH_3), 2.86-2.82 (m, 2H, C_6-2H), 2.72-2.68 (m, 2H, C_5-2H); Anal. calcd. for: $C_{25}H_{18}N_4O$. Found: C, 76.79; H, 4.69; N, 14.25 %.

General procedure for the preparation of spiro[indoline-3',4-benzo[*a*]carbazole 13

A magnetically stirred mixture of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (1.0 mmol), malononitrile **2** (1.0 mmol), isatin **11** (1.0 mmol) and the DABCO (0.5 mmol) in dry ethanol (15.0 mL). The reaction mixture was constant stirring 30 min and the progress of the reaction was monitored by checking TLC time to time, the solid precipitate appeared slowly at the end of the reaction. Then, the precipitate was just filtered and it was washed with dry ethnol (3 x 5 mL), and it was dried to give pure compound.

2-Imino-8-methyl-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13a): Pale yellow solid; yield: 366 mg (83%); m.p. 222-224 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3452 (indol, NH), 3383 (oxoindol, NH), 3279 (imino NH) and 2219 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.58 (b s, 1H, C_{11}-NH), 11.36 (b s, 1H, C_1'-NH), 10.93 (b s, 1H, C_2-NH imino), 7.53 (d, 1H, C_{10}-H, J_o = 8.0 Hz), 7.41-7.37 (m, 1H, C_6'-H, J_o = 7.6 Hz), 7.35 (s, 1H, C_7-H), 7.22 (d, 1H, C_7'-H, J_o = 7.6 Hz), 7.06 (d, 1H, C_4'-H, J_o = 7.6 Hz), 7.02 (t, 1H, C_5'-H, J_o = 7.6 Hz), 6.96 (d, 1H, C_9-H, J_o = 8.0 Hz), 3.70 (d d, 1H, C_{4a}-H, J_{cis} = 3.2 Hz & J_{trans} = 12.0 Hz), 2.98-2.95 (m, 2H, C_6-H), 2.34 (s, 3H, CH_3), 1.69-1.66 (m, 1H, C_{5b}-H), 1.32-1.28 (m, 1H, C_{5a}-H); ^{13}C NMR(100 MHz, DMSO) (ppm) δ_C: 173.4 (C=O), 156.5 (C_{11b}), 149.4 (C_2), 143.3 (C_{7a}'), 139.8 (C_{3a}'), 131.7 (C_{11a}), 130.8 (C_{10a}), 130.2 (C_8), 130.0 (C_6'), 128.1 (C_{6b}), 126.1 (C_5'), 125.8 (C_4'), 123.5 (C_9), 122.0 (C_7), 120.2 (CN), 115.5 (CN), 113.9 (CN), 111.7 (C_{6a}), 111.2 (C_{10}), 110.8 (C'$_7$), 93.8 (C_1), 55.1 (C_4), 48.0 (C_{4a}), 26.6 (C_3), 21.3 (C_6), 21.1 (C_5), 18.9 (CH_3); Anal. calcd. for: $C_{27}H_{18}N_6O$: C, 73.29; H, 4.10; N, 18.99. Found: C, 73.20; H, 4.15; N, 18.92 %.

2-Imino-10-methyl-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13b): Pale yellow solid; yield: 358 mg (81%); m.p. 223-225 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3449 (Indole, NH), 3408 (oxoindole, NH), 3262 (imino, NH), 2214 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.24 (b s, 1H, C_{11}-NH), 10.28 (b s, 1H, C_1'-NH), 9.79 (b s, 1H, C_2-NH imino), 7.31 (d, 1H, C_7-H, J_o = 8.0 Hz), 7.27-7.23 (m, 1H, C_7'-H), 7.12 (d, 1H, C_4'-H, J_o = 7.2 Hz), 6.98-6.94 (m, 2H, C_6' & C_5'-H), 6.88-6.84 (m, 2H, C_9 & C_8-H), 3.73-3.68 (m, 1H, C_{4a}-

H), 3.01-2.84 (m, 2H, C_6-H), 2.44 (s, 3H, CH_3), 1.78-1.75 (m, 1H, C_{5b}-H), 1.39-1.31 (m, 1H, C_{5a}-H); ^{13}C NMR(100 MHz, DMSO) (ppm) δ_C: 173.3 (C=O), 156.6 (C_{11b}), 149.7 (C_2), 143.3 (C_{7a}'), 140.8 (C_{3a}'), 131.8 (C_{11a}), 131.0 (C_{10a}), 128.8 (C_8), 128.5 (C_6'), 126.0 (C_{6b}), 125.8 (C_5'), 123.5 (C_4'), 122.7 (C_9), 122.0 (C_7), 121.7 (CN), 185.9 (CN), 115.9 (CN), 111.7 (C_{6a}), 111.2 (C_{10}), 110.8 (C'$_7$), 94.7 (C_1), 55.1 (C_4), 48.0 (C_{4a}), 26.7 (C_3), 21.3 (C_6 & C_5), 16.6 (CH_3); Anal. calcd. for: $C_{27}H_{18}N_6O$: C, 73.29; H, 4.10; N, 18.99. Found: C, 73.37; H, 4.06; N, 18.93 %.

2-Imino-8-chloro-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13c): Pale yellow solid; yield: 364 mg (79%); m.p. 225-227 °C; FT-IR (KBr, cm^{-1}) ν_{max}:3422 (Indole NH), 3380 (oxoindole NH), 3277 (imino NH), 2223 (CN). ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.75 (b s, 1H, C_{11}-NH), 11.73 (b s, 1H, C_1'-NH), 10.59 (b s, 1H, C_2-NH imino), 7.50-7.47 (m, 2H, C_7 & C_6'-H), 7.44 (d, 1H, C_{10}-H, J_o = 8.4 Hz), 7.21 (d, 1H, C_7'-H, J_o = 7.6 Hz), 7.10 (d, 1H, C_9-H, J_o = 8.4 Hz), 7.04 (t, 1H, C_5-H, J_o = 7.6 Hz), 6.96-6.95 (m, 1H, C_4'-H), 3.74 (d d, 1H, J_{cis} = 3.6 Hz & J_{trans} = 12.4 Hz), 3.02-3.00 (m, 2H, C_6-H), 1.70-1.68 (m, 1H, C_{5b}-H), 1.41-1.39 (m, 1H, C_{5a}-H); Anal. calcd. for: $C_{26}H_{15}ClN_6O$: C, 67.46; H, 3.27; N, 18.16; Found: C, 67.51; H, 3.22; N, 18.09 %.

2-Imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13d): Pale yellow solid; yield: 342 mg (80%); m.p. 223-225 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3450 (Indole NH & oxoindole NH), 3248 (imino NH), 2210 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.57 (b s, 1H, C_{11}-NH), 11.41 (b s, 1H, C_1'-NH), 10.99 (b s, 1H, C_2-NH imino), 7.67-7.61 (m, 1H, C_7-H), 7.58 (d, 1H, C_7'-H, J_o = 8.4 Hz), 7.41-7.36 (m, 2H, C_{10} & C_4'-H), 7.13-6.90 (m, 4H, C_9, C_8, C_6' & C_5'-H), 3.72 (d d, 1H, C_{4a}-H, J_{cis} = 3.4 Hz & J_{trans} = 12.4 Hz), 3.02-2.92 (m, 2H, C_6-H), 1.70-1.96 (m, 1H, C_{5b}-H), 1.34-1.28 (m, 1H, C_{5a}-H). Anal. Calcd. For: $C_{26}H_{16}N_6O$: C, 72.89; H, 3.76; N, 19.62. Found: C, 72.81; H, 3.81; N, 19.57 %.

5'-Fluoro-2-imino-8-methyl-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13e): Pale yellow solid; yield: 340 mg (74%); m.p. 224-226 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3416 (Indole NH & oxoindole NH), 3239 (imino, NH), 2211 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 10.56 (b s, 1H, C_{11}-NH), 9.53 (b s, 1H, C_2-NH imino), 8.31 (b s, 1H, C_1'-NH), 7.45-7.30 (m, 2H, C_7 & C_{10}-H), 7.10-6.99 (m, 4H, C_9, C_7', C_6' & C_4'-H), 3.68 (d d,

1H, C_{4a}-H, J_{cis} = 3.6 Hz & J_{trans} = 12.8 Hz), 3.11-2.96 (m, 2H, C_6-H), 2.54 (s, 3H, CH_3), 1.92-1.89 (m, 1H, C_{5b}-H), 1.49-1.45 (m, 1H, C_{5a}-H); ^{13}C NMR(100 MHz, DMSO) (ppm) δ_C: 173.3 (C=O), 156.6 (C_{11b}), 149.7 (C_2), 143.3 (C_{7a}'), 140.8 (C_{3a}'), 131.8 (C_{11a}), 131.0 (C_{10a}), 128.8 (C_8), 128.5 (C'$_6$), 126.0 (C_{6b}), 125.8 (C_5'), 123.5 (C_4'), 122.7 (C_9), 122.0 (C_7), 121.7 (CN), 118.9 (CN), 115.9 (CN), 111.7 (C_{6a}), 111.2 (C_{10}), 110.8 (C_7'), 94.8 (C_1), 55.1 (C_4), 48.0 (C_{4a}), 26.7 (C_3), 21.1 (C_6 & C_5), 16.6 (CH_3); Anal. calcd. for: $C_{27}H_{17}FN_6O$:C, 70.43; H, 3.72; N, 18.25. Found: 70.51; H, 3.68; N, 18.19 %.

5'-Fluoro-2-imino-10-methyl-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13f): Pale yellow solid; yield: 349 mg (76%); m.p. 225-227 °C; FT-IR (KBr, cm^{-1}) $\nu_{max:}$ 3453 (Indole NH), 3345 (oxoindole NH), 3276 (imino, NH), 2209 (CN). ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.19 (b s, 1H, C_{11}-NH), 9.77 (b s, 1H, C_2-NH imino), 7.22 (d, 1H, C_7-H, J_o = 8.0 Hz), 7.11-7.09 (m, 2H, C_8 & C_6'-H), 7.04 (d, 1H, C_7'-H, J_o = 8.0 Hz), 6.81 (d, 1H, C_9-H, J_o = 8.0 Hz), 6.65 (d, 1H, C_4'-H, J_m = 2.0 Hz), 3.58 (d d, 1H, C_{4a}-H, J_{cis} = 3.2 Hz & J_{trans} = 12.4 Hz), 2.88-2.83 (m, 1H, C_{6b}-H), 2.77-2.74 (m, 2H, C_{6a}-H), 2.19 (s, 3H, CH_3), 1.66-1.62 (m, 1H, C_{5b}-H), 1.26-1.19 (m, 1H, C_{5a}-H); Anal. calcd. for: $C_{27}H_{17}FN_6O$: C, 70.43; H, 3.72; N, 18.25. Found: 70.51; H, 3.77; N, 18.30 %.

8-Chloro-5'-fluoro-2-imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13g): Pale yellow solid; yield: 340 mg (71%); m.p. 220-222 °C; FT-IR (KBr, cm^{-1}) $\nu_{max:}$ 3425 (Indole NH & oxoindole NH), 3249 (imino, NH), 2205 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.87(b s, 1H, C_{11}-NH), 11.77 (b s, 1H, C_2-NH imino), 11.21 (b s, 1H, C_1'-NH), 7.69-7.65 (m, 2H, C_7 & C_{10}-H), 7.48 (d, 1H, C_6'-H, J_m = 1.6 Hz & J_o = 8.6 Hz), 7.36 (d d, 1H, C_9-H, J_m = 2.4 Hz & J_o = 8.4 Hz), 7.11-7.08 (m, 1H, C_7-H, 6.97 (d, 1H, C_4'-H, J_m = 1.6 Hz), 3.71 (d d, 1H, C_{4a}-H, J_{cis} = 3.4 Hz & J_{trans} = 12.4 Hz), 3.01-2.91 (m, 2H, C_6-H), 1.67-1.64 (m, 1H, C_{5b}-H), 1.44-1.39 (m, 1H, C_{5a}-H); Anal. calcd. for: $C_{26}H_{14}ClFN_6O$: C, 64.94; H, 2.93; N, 17.48. Found: C, 64.85; H, 2.98; N, 17.43 %.

5'-Fluoro-2-imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13h): Pale yellow solid; yield: 356 mg (80%); m.p. 223-225 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3442 (Indole NH), 3390 (oxoindole NH), 3258 (imino, NH), 2213 (CN); ^{1}H NMR

(400 MHz, $CDCl_3$) (ppm) δ_H: 11.64 (b s, 1H, C_{11}-NH), 11.45 (b s, 1H, C_2-NH imino), 11.00 (b s, 1H, C_1'-NH), 7.65 (d, 1H, C_7-H, J_o = 8.4 Hz), 7.60 (d, 1H, C_6'-H, J_o = 8.0 Hz), 7.38 (t, 1H, C_8-H, J_o = 8.4 Hz), 7.29-7.25 (m, 1H, C_7'-H), 7.12-7.07 (m, 2H, C_{10} & C_9-H), 6.89 (d, 1H, C_4'-H, J_m = 2.0 Hz), 3.71 (d d, 1H, C_{4a}-H, J_{cis} = 3.2 Hz & J_{trans} = 12.8 Hz), 3.02-3.01 (m, 2H, C_6-H), 1.69-1.67 (m, 1H, C_{5b}-H), 1.42-1.38 (m, 1H, C_{5a}-H); Anal. calcd. for: $C_{26}H_{15}FN_6O$: C, 69.95; H, 3.39; N, 18.82. Found: C, 69.84; H, 3.35; N, 18.89 %.

5'-Chloro-2-imino-8-methyl-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13i): Pale yellow solid; yield: 409 mg (86%); m.p. 220-222 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3491 (Indole NH), 3376 (oxoindole NH), 3282 (imino, NH), 2214 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.38 (b s, 1H, C_{11}-NH), 10.11 (b s, 1H, C_2-NH imino), 7.37 (d, 1H, C_{10}-H, J_o = 8.8 Hz), 7.24-7.22 (m, 2H, C_7 & C_6'), 7.16-7.13 (m, 1H, C_9-H), 6.93 (d, 1H, C_7'-H, J_o = 8.4), 6.77 (d, 1H, C_4'-H, J_m = 1.6 Hz), 3.68 (d d, 1H, C_{4a}-H, J_{cis} = 3.6 Hz & J_{trans} = 12.2 Hz), 3.01-2.95 (m, 1H, C_{6b}-H), 2.90-2.82 (m, 1H, C_{6a}-H), 2.31 (s, 3H, CH_3), 1.77-1.73 (m, 1H, C_{5b}-H), 1.39-1.34 (m, 1H, C_{5a}-H); ^{13}C NMR(100 MHz, DMSO) (ppm) δ_C: 173.0 (C=O), 142.4 (C_{11b} & C_2), 132.0 (C_{7a}' & C_{3a}'), 128.8 (C_{11a}), 128.5 (C_5'), 127.4 (C_{10a} & C_8), 126.0 (C_6 '& C_4'), 125.6 (C_{6b} & C_9), 123.8 (C_7 & C_{6a}), 122.7 (C_7'), 121.7 (CN), 119.0 (CN & CN), 113.3 (C_{10} & C_1), 60.1 (C_4), 55.4 (C_{4a}), 26.6 (C_3), 21.1 (C_6 & C_5), 16.6 (CH_3); Anal. calcd. for: $C_{27}H_{17}ClN_6O$: C, 68.00; H, 3.59; N, 17.62. Found: C, 68.09; H, 3.55; N, 17.68 %.

5'-Chloro-2-imino-10-methyl-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13j): Pale yellow solid; yield: 390 mg (83%); m.p. 221-223 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3455 (Indole NH), 3372 (oxoindole NH), 3287 (imino, NH), 2208 (CN). ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.75 (b s, 1H, C_{11}-NH), 11.57 (b s, 1H, C_2-NH imino), 10.61 (b s, 1H, C_1'-NH), 7.49 (d d, 1H, C_6'-H, J_m = 2.0 Hz & J_o= 8.6 Hz), 7.44 (d, 1H, C_7-H, J_o = 8.4 Hz), 7.21 (d, 1H, C_7'-H, J_o = 8.4 Hz), 7.10 (d, 1H, C_9-H, J_o = 8.4 Hz), 7.04 (t, 1H, C_8-H, J_o = 8.4 Hz), 6.90 (d, 1H, C_4'-H, J_m = 2.0 Hz), 3.74 (d d, 1H, C_{4a}-H, J_{cis} = 3.6 Hz & J_{trans} = 12.8 Hz), 3.01-3.00 (m, 2H, C_6-H), 2.47 (s, 3H, CH_3), 1.71-1.67 (m, 1H, C_{5b}-H), 1.44-1.38 (m, 1H, C_{5a}-H). Anal. calcd. for: $C_{27}H_{17}ClN_6O$: C, 68.00; H, 3.59; N, 17.62. Found: C, 68.09; H, 3.63; N, 17.68 %.

5',8-Dichloro-2-imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13k): Pale yellow solid; yield: 441 mg (90%); m.p. 219-221 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3405 (Indole NH), 3376 (oxoindole NH), 3278 (imino, NH), 2225 (CN); ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.77 (b s, 1H, C_{11}-NH), 11.65 (b s, 1H, C_2-NH imino), 11.21 (b s, 1H, C_1'-NH), 7.69-7.66 (m, 2H, C_{10} & C_7-H), 7.49 (d d, 1H, C_6'-H, J_m = 2.4 Hz & J_o = 8.4 Hz), 7.37 (d d, 1H, C_9-H, J_m = 2.0 Hz & J_o = 8.8 Hz), 7.11-7.08 (m, 1H, C_7'-H), 6.98 (d, 1H, J_m = 1.6 Hz), 3.73 (d d, 1H, C_{4a}-H, J_{cis} = 3.2 Hz & J_{trans} = 12.8 Hz), 3.04-2.92 (m, 2H, C_6-H), 1.67-1.64 (m, 1H, C_{5b}-H), 1.44-1.39 (m, 1H, C_{5a}-H); Anal. calcd. for: $C_{26}H_{14}Cl_2N_6O$: C, 62.79; H, 2.84; N, 16.90. Found: C, 62.71; H, 2.79; N, 16.96 %.

5'-Chloro-2-imino-2'-oxo-5,6-dihydro-11*H*-spiro[indoline-3',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (13l): Pale yellow solid; yield: 392 mg (85%); m.p. 223-225 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3442 (Indole NH), 3378 (oxoindole NH), 3257 (imino, NH), 2213 (CN). ^{1}H NMR (400 MHz, DMSO) (ppm) δ_H: 11.75 (b s, 1H, C_{11}-NH), 11.53 (b s, 1H, C_2-NH imino), 11.02 (b s, 1H, C_1'-NH), 7.64 (d, 1H, C_7-H, J_o = 8.4 Hz), 7.59 (d, 1H, C_{10}-H, J_o = 8.4 Hz), 7.48 (d d, 1H, C_6'-H, J_m = 1.6 Hz & J_o = 8.4 Hz), 7.38 (t, 1H, C_8-H, J_o = 8.4 Hz), 7.12-7.08 (m, 2H, C_9 & C_7'-H), 6.97 (d, 1H, C_4'-H, J_m = 1.6 Hz), 3.74 (d d, 1H, C_{4a}-H, J_{cis} = 3.2 Hz & J_{trans} = 12.0 Hz), 3.02-2.98 (m, 2H, C_6-H), 1.69-1.66 (m, 1H, C_{5b}-H), 1.43-1.39 (m, 1H, C_{5a}-H); Anal. calcd. for: $C_{26}H_{15}ClN_6O$: C, 67.46; H, 3.27; N, 18.16. Found: C, 67.54; H, 3.24; N, 18.22 %.

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Supplementary data

Crystallographic data for compounds **4a**, **7d, 10l** and **13b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1531718-1531721. Copies of the data can be obtained free of charge on application to CCDC, 12 Union

Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk]. Spectral data of all the compounds are associated with this article will be available as supporting information

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