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Article

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Substrate Controlled Regio- and Stereoselective Synthesis of (*Z*) and (*E*) *N*–Styrylated Carbazoles, Aza–Carbazoles and γ–Carbolines *via* Hydroamination of Alkynes

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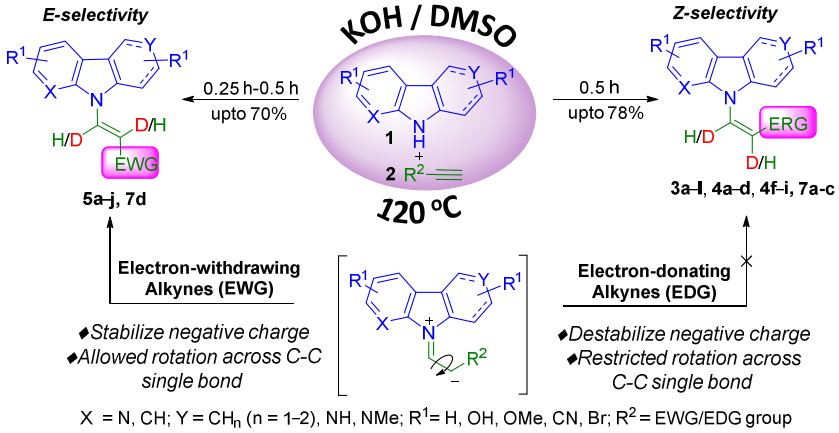


ABSTRACT: We report herein the substrate controlled regio- and stereoselective hydroamination of carbazoles, aza–carbazoles and γ–carbolines with functionalized aromatic as well as aliphatic alkynes in KOH/DMSO system in good yields. The electronic effect of the substrates governs the stereochemistry of the product. Electron–donating alkynes provided (*Z*)–stereoselective products and electron–withdrawing alkynes provided (*E*)–stereoselective products. This approach also provides an easy route for the synthesis of mono and bis–

hydroaminated product. The deuterium labeling studies were also conducted to support the mechanistic pathway.

INTRODUCTION

Carbazole, discovered over century ago[1, 2] is a privileged heterocyclic motif, and its analogs exhibit plentiful applications due to unique structural and electronic features. Most importantly, the abundance of carbazoles in natural product and medicines, made them highly demanding due to their versatile implications as anti-tumor,[3a] anti–oxidative,[3b] anti–inflammatory,[3c] and anti–mutagenic agents.[3d] During the past few decades, aza–carbazoles and γ–carbolines have attracted a huge interest of chemists relatively due to the broad spectrum of their biological activity.[4-6] Aza–carbazole nucleus are found in many natural alkaloids such as neocryptolepine and, they have the ability to interact with DNA as intercalators to inhibit the topoisomerase II activity.[7] *N*-Alkylated γ–Carbolines are present in biologically active antihistamine drug molecules such as latrepirdine or dimebon **A** (a marketed drug) (Figure 1).[8]

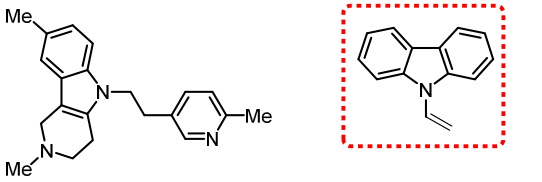


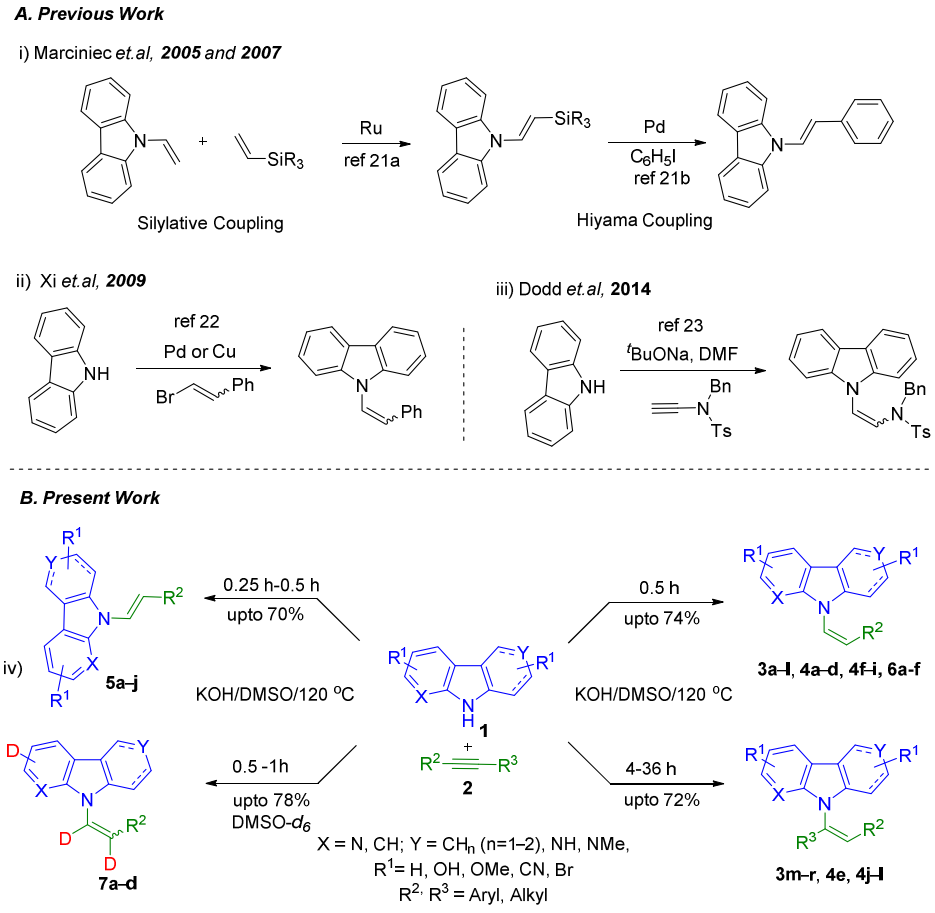
Figure 1. Biologically active core of carbazole derivatives

The distinctive electronic environment of carbazoles and their analogs made them widely susceptible key motifs in the development of organic light–emitting materials.[9] These are potential candidates for electronic devices, such as color display, organic semiconductor lasers, solar cells, etc.[10] Further the styrylated derivatives of carbazoles (**B**) are used in polymer

chemistry due to the tendency of alkenes to undergo polymerization and leading to polyvinyl carbazoles (PVC) (Figure 1).[11]

Owing to the widespread application of carbazole analogs, various methods have been developed for their synthesis.[12] The *N*–functionalized carbazoles are in high demand as their solubility in water, or organic solvents have been a major concern, which strongly depends on *N*–substituted hydrophilic or hydrophobic chain. The *N*–alkenylation of heterocycles has been well reported using transition–metal catalyst,[13-19] however, the regio– and stereoselective C–N bond formation reaction are in high demand.[20]

Scheme 1. Synthesis of *N*–alkenylated Carbazoles



In 2005 and 2007 Marciniec group investigated the sequential silylative and Hiyama coupling for the synthesis of styryl carbazoles[21a-b] using ruthenium and palladium complexes respectively (Scheme 1, i). Later on, the copper-catalyzed coupling of vinyl halides with carbazoles was reported by Xi and co-workers in 2009 for the formation of corresponding vinylated carbazoles[22] (Scheme 1, ii). In 2014, Dodd *et al.*, synthesized the *N*–vinylated heterocycles including carbazole[23] by employing ynamides as a coupling partner (Scheme 1, iii). In continuation of our ongoing research on *N*–alkenylation of heterocycles[20b] and our interest in the carbazole synthesis,[24a-c] herein we have designed the substrate controlled regio– and stereoselective synthesis of (*Z*) and (*E*) *N*–styryl carbazoles, aza–carbazoles and γ–carbolines *via* hydroamination of alkynes in presence of KOH/DMSO (Scheme 1, iv).

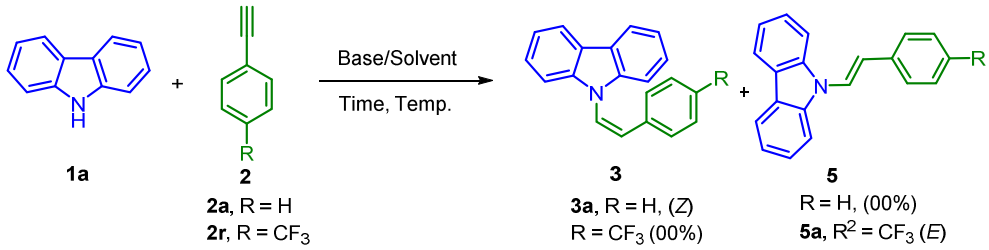
RESULTS AND DISCUSSION

In order to obtain the stereoselectivity of the products, various reaction conditions were examined using carbazole **1a** as our model substrate (Table 1). Initially, we treated phenyl acetylene **2a** with carbazole **1a**, using our previous reported condition that is KOH (0.5 equiv) in DMSO at 120 °C for 0.5 h.[25] Gratifyingly, the (*Z*)–styryl product **3a** was obtained in 74% yield (Table 1, entry 1). Inferior results were obtained by altering the amount of base (entries 2 and 3). In order to attain (*E*)–selective product, the reaction was allowed to run from 2 to 24 h using 0.5 equiv of KOH however; no change in the stereochemistry of the product **3a** was obtained (entries 4–7). Further, increasing the amount of base and reaction time also provided the (*Z*)–stereoselective product **3a** in moderate yields (entries 8–10). Next, to get the optimal temperature, we perform the reaction at 100 ^{o}C and 80 ^{o}C, however; the product **3a** was observed in 56% and 48% yields, respectively (entries 11-12). No product was observed on further carrying the reaction up to room temperature (entries 13-14). Further, to obtained the stereoselective (*E*) product, we

employed an electron-withdrawing alkyne; 1-ethynyl-4-(trifluoromethyl)benzene **2r** with **1a** using 0.5 equiv of KOH, product **5a** was obtained in 65% yield (entry 15). To control the stereochemistry of the product, the amount of base as well as temperature was decreased; however the *E*-isomer **5a** was obtained instead of *Z*-isomer **3a** (entries 16–17). No improvement was observed in the yield of the product **5a** on increasing the equivalent of KOH (entries 18–19).

Other bases such as NaOH, $CsOH.H_2O$, and KO^tBu provided the desired product **3a** in lower yields (entries 20–22). However, organic base (Et_3N) failed to provide the hydroaminated product **3a** (entry 23). Therefore, (entry 1) 0.5 equiv of KOH in DMSO at 120 °C for 0.5 h with electron-donating alkyne was chosen as the optimal reaction conditions for the synthesis of (*Z*)–styrylated carbazole **3a** and 0.5 equiv of KOH in DMSO at 120 °C for 0.5 h with electron-withdrawing alkyne for the synthesis of (*E*)–styrylated carbazole **5a** (entry 15).

Table 1. Optimization of the Reaction Conditions[a]



entry	alkyne	base (equiv)	solvent	time (h)/*T* °C	yield (%)[b] **3a/5a** (*Z*:*E*)
1	**2a**	**KOH (0.5)**	**DMSO**	**0.5 / 120**	**74 (100:00)**
2	**2a**	KOH (1.0)	DMSO	0.5 / 120	68 (100: 00)
3	**2a**	KOH (0.2)	DMSO	0.5 / 120	60 (100:00)
4	**2a**	KOH (0.5)	DMSO	2.0 / 120	74 (100:00)
5	**2a**	KOH (0.5)	DMSO	8.0 / 120	70 (100:00)
6	**2a**	KOH (0.5)	DMSO	12 / 120	70 (100:00)

7	**2a**	KOH (0.5)	DMSO	24 / 120	70 (100:00)
8	**2a**	KOH (1.0)	DMSO	24 / 120	68 (100: 00)
9	**2a**	KOH (2.0)	DMSO	30 / 120	68 (100:00)
10	**2a**	KOH (4.0)	DMSO	30 / 120	65 (100:00)
11	**2a**	KOH (0.5)	DMSO	0.5 / 100	56 (100: 00)
12	**2a**	KOH (0.5)	DMSO	0.5 / 80	48 (100: 00)
13	**2a**	KOH (0.5)	DMSO	0.5 / 60	NR
14	**2a**	KOH (0.5)	DMSO	24 / 25	NR
15	**2r**	**KOH (0.5)**	**DMSO**	**0.5 / 120**	**65 (00:100)**
16	**2r**	KOH (0.2)	DMSO	0.5 / 120	55 (00:100)
17	**2r**	KOH (0.2)	DMSO	0.5 / 80	40 (00:100)
18	**2r**	KOH (1.0)	DMSO	0.5 / 120	60 (00:100)
19	**2r**	KOH (2.0)	DMSO	0.5 / 120	48 (00:100)
20	**2a**	NaOH (0.5)	DMSO	0.5 / 120	69 (100:00)
21	**2a**	$CsOH.H_2O$ (0.5)	DMSO	1.0 / 120	62 (100:00)
22	**2a**	KO^tBu (0.5)	DMSO	1.0 / 120	60 (100:00)
23	**2a**	Et_3N (0.5)	DMSO	24 / 120	NR

[a]Reactions were performed using carbazole **1a** (0.5 mmol), alkyne **2a/2r** (0.5 mmol) in 2.0 mL of DMSO. [b]Yield.

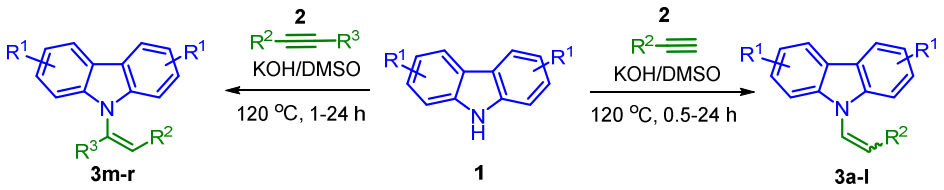
After optimizing the reaction conditions, we synthesized a variety of styrylated carbazole derivatives **3a–l** with aromatic terminal alkynes using 0.5 equiv KOH at 120 ^oC for 0.5 h (Table 2). The reaction of substrate **1a** with phenylacetylene **2a** and 1-butyl-4-ethynylbenzene **2b** provided the desired products **3a–b** in good yields (entries 1 and 2). Similarly, the reaction of carbazole **1a**

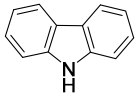
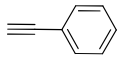
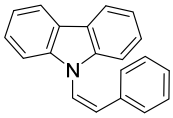
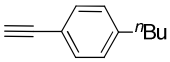
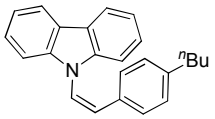
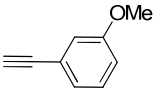
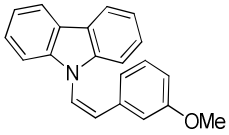
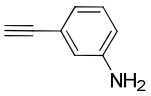
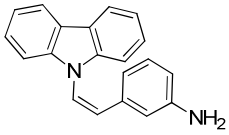
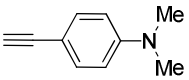
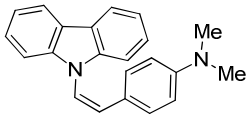
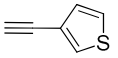
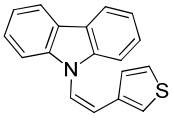
with alkyne **2c** afforded the hydroaminated product **3c** in 70% yield (entry 3). Significantly, 3-ethynylaniline **2d** and 4-ethynyl-*N*, *N*-dimethylaniline **2e** afforded the desired products **3d** and **3e** in 68% and 69% yields, respectively (entries 4 and 5). When the reaction was performed using electron-rich alkyne 3-ethynylthiophene **2f**, the desired product **3f** was obtained in 65% yield (entry 6). We next extended the substrate scope by employing substituted carbazoles bearing hydroxy and a methoxy group at C–2 position. Chemoselective addition of 2–hydroxycarbazole **1b** on to 1-ethynyl-3-methoxybenzene **2c** provided the mixture of isomers **3g** (*Z*/*E* = 40:60) in 70% yield (entry 7), however; the reaction of 2–methoxy carbazole **1c** with electron neutral alkyne **2a** provided the corresponding *Z*-addition product **3h** in 72% yield (entry 8). The formation of the mixture of isomers in **3g** as compare to single isomer in **3h**, might be due to the presence of methoxy group on meta position on the alkyne which creates steric hindrance with the hydroxyl group of carbazole. Interestingly, halogen substituted carbazole **1d** gave the addition products **3i**–**j** in 69% and 71% yields, respectively (entries 9 and 10). Carbazole bearing electron-withdrawing groups such as **1e** and **1f** were also capable of providing the hydroaminated product **3k**–**l** in good yields (entries 11 and 12).

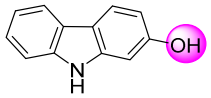
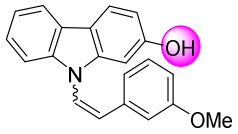
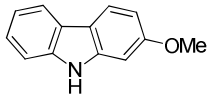
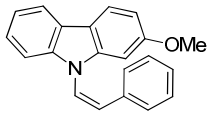
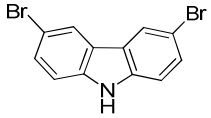
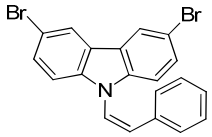
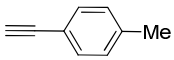
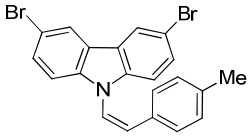
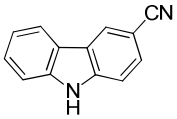
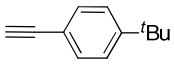
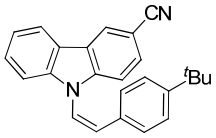
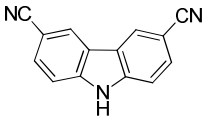
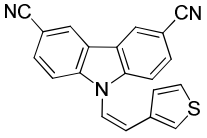
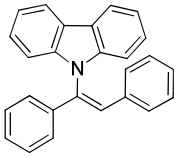
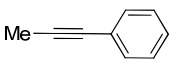
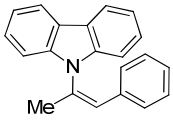
To further extend the scope and generality of protocol, various symmetrical and unsymmetrical internal alkynes were explored with electronically varied carbazoles **1a**–**b** to afford the *N*-styryl carbazoles **3m**–**r** in good yields with excellent regioselectivity. The reaction of **1a** with diphenylacetylene **2i** gave the desired product **3m** in 70% yield (entry 13). Next, when **1a** was reacted with unsymmetrical internal alkyne **2j** and **2k**, the products **3n** and **3o** were obtained in 70 and 68% yields, respectively (entries 14 and 15). Carbazoles **1a** reacted with a highly electron-withdrawing group having 3-((4-nitrophenyl)ethynyl)thiophene **2l** to afford the corresponding product **3p** in 67% yield (entry 16). Diphenylacetylene **2i** reacted smoothly with 9*H*-carbazol-2-ol

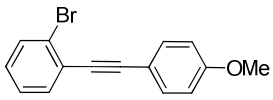
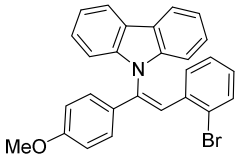
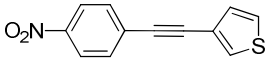
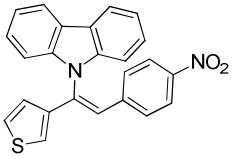
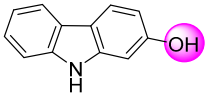
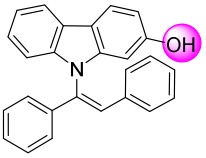
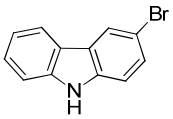
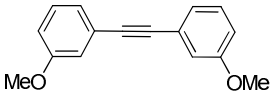
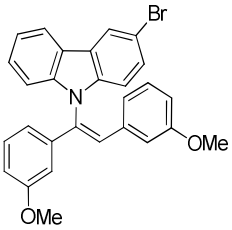
1b and we obtained the product **3q** in 62% yield, without affecting the hydroxy group (entry 17). The reaction of 3-bromo-9*H*-carbazole **1g** with symmetrical alkyne **2m** provided the desired product **3r** in 65% yield (entry 18).

Table 2. Scope of Carbazoles with Terminal and Internal Alkynes[a]



entry	carbazoles	alkyne **2**	product **3**	yield (%)
1	 **1a**	 **2a**		**3a**	74
2	**1a**	 **2b**		**3b**	70
3	**1a**	 **2c**		**3c**	70
4	**1a**	 **2d**		**3d**	68
5	**1a**	 **2e**		**3e**	69[b]
6	**1a**	 **2f**		**3f**	65

7	 **1b**		**2c**	 (*Z*:*E*::40:60)	**3g**	70
8	 **1c**		**2a**		**3h**	72
9	 **1d**		**2a**		**3i**	69
10	**1d**		**2g**		**3j**	71
11	 **1e**		**2h**		**3k**	68
12	 **1f**		**2f**		**3l**	65
13	**1a**		**2i**		**3m**	70 [c]
14	**1a**		**2j**		**3n**	70 [c]

15	**1a**		**2k**		**3o**	68 [c]
16	**1a**		**2l**		**3p**	67 [c]
17	 **1b**		**2i**		**3q**	62 [c]
18	 **1g**		**2m**		**3r**	65 [c]

[a]The reactions were performed using carbazole **1** (0.5 mmol), 0.5 mmol of alkyne **2**, 0.5 equiv of KOH in 2.0 mL of DMSO at 120 °C for 0.5 h. [b]24 h. [c]1.5 equiv of KOH for 24 h.

It is important to note that the electronic nature of the groups on the alkynes play a key role for the high regioselectivity of the reaction (Figure 2). The presence of electron-donating and electron-withdrawing group on the triple bond decreases the electron density on carbon (C_a) and increases on carbon (C_b) of the triple bond.[26] Owing to this electronic effect, the nucleophile (*N*-heterocyclic) attacks on positively charged carbon centre (C_a) to provide the regioselective products. The regioselectivity of the reaction was further recognized by NOESY studies (see ESI).

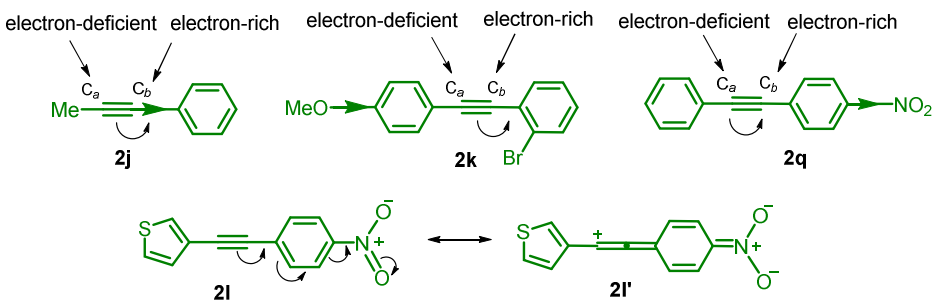


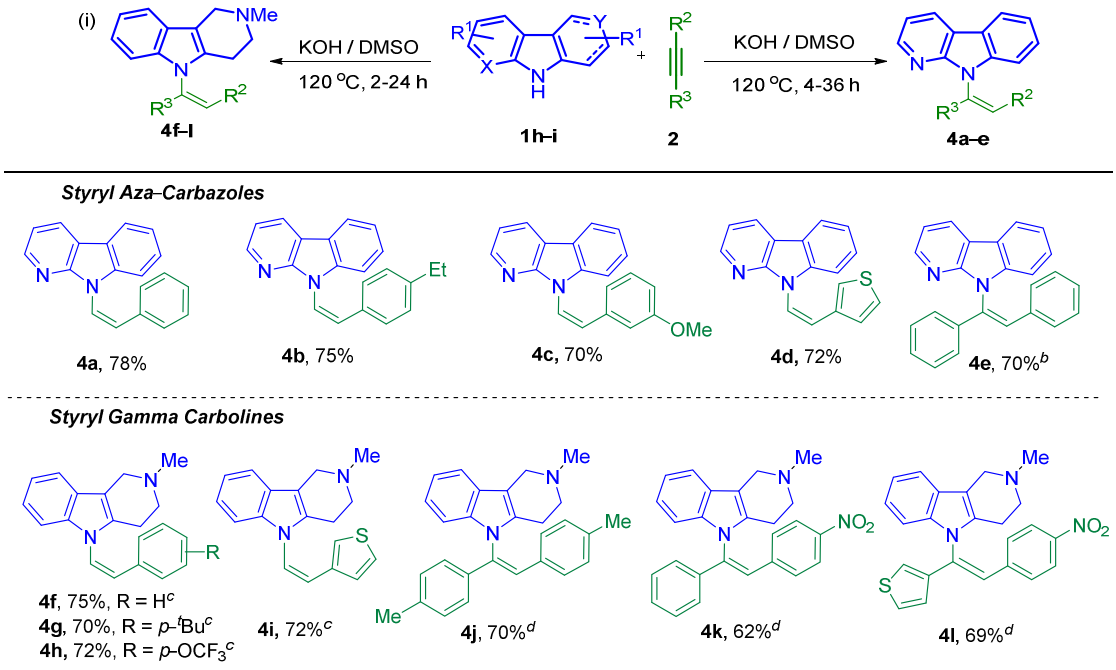
Figure 2. Electronic effect of substituents in unsymmetrical internal alkynes

Next, we explore the scope of the reaction by using aza–carbazoles **1h** with alkynes **2** for the synthesis of *Z*-selective isomer **4a–e** in good yields (Scheme 2). The aza–carbazole **1h** reacted with phenylacetylene **2a** to afford the corresponding product **4a** in 78% yield. The reaction with electron donating alkynes such as of 1-ethyl-4-ethynylbenzene **2n** and 1-ethynyl-3-methoxybenzene **2c** with aza-carbazole **1h** provided the addition product **4b–c** in 75% and 70% yields, respectively. The heteroalkyne **2f** was well tolerated in the reaction to gave the hydroaminated product **4d** in good yield. Interestingly, aza–carbazole **1h** was successfully reacted with internal alkyne diphenylacetylene **2i** using 1.5 equiv of KOH at 120 ^{o}C for 36 h, to afford the desired product **4e** in 70% yield.

In continuation, we extended the reaction by taking biologically active gamma–carbolines **1i** with terminal and internal alkynes **2** to synthesize the styrylated product **4f-l** in good yields (Scheme 2). The addition of gamma–carbolines **1i** on alkyne **2a** by using KOH (0.5 equiv) at 120 ^{o}C for 4 h, leads to the formation of (*Z*)-9-styryl-9*H*-pyrido[2,3-*b*]indole **4f** in 75% yield. When the reaction of **1i** was carried out with 1-(*tert*-butyl)-4-ethynylbenzene **2h** and 1-ethynyl-4-(trifluoromethoxy)benzene **2o**, the corresponding products **4g** and **4h** were obtained in 70% and 72% yields, respectively. The thienyl ring containing alkyne **2f** gave the desired product **4i** in 72% yield. The successful addition of the gamma–carbolines onto

terminal alkynes encouraged us for the addition of **1i** onto symmetrical and unsymmetrical internal alkynes. The reaction of 1, 2-di-*p*-tolylethyne **2p** with **1i** provided the hydroaminated product **4j** in 70% yield. Electron-withdrawing alkyne such as 1-nitro-4-(phenylethynyl)benzene **2q** and 3-((4-nitrophenyl)ethynyl)thiophene **2l** also provided the regioselective styryl gamma carbolines **4k–l** in good yields (see Figure 2).

Scheme 2. Hydroamination on Alkynes using Aza-Carbazole and γ–Carboline[a]

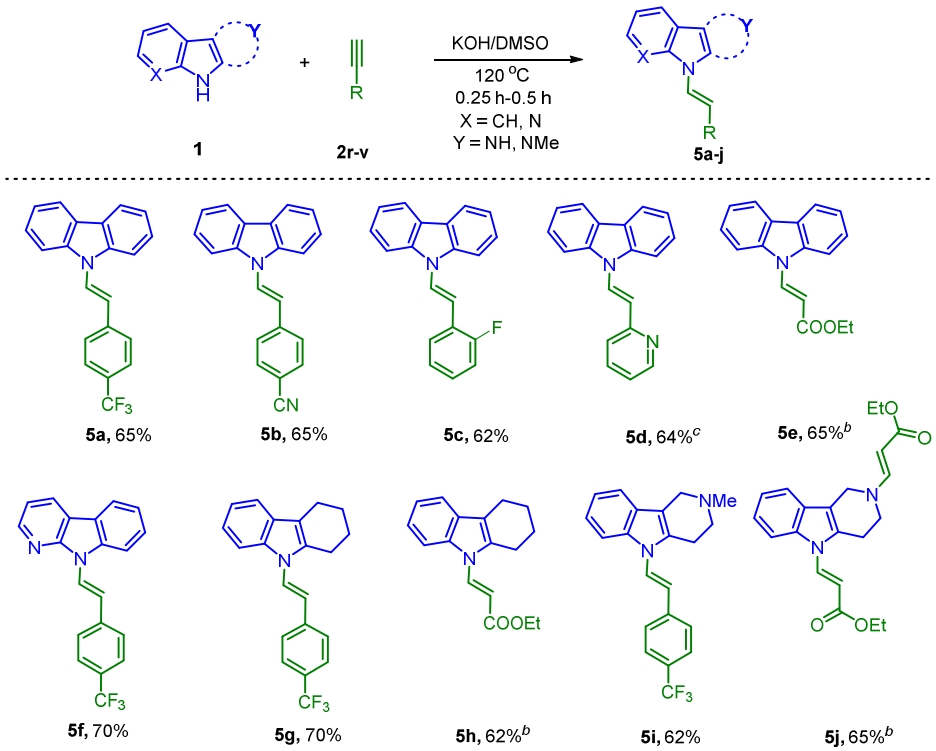


[a]The reactions were performed using *N*–heterocycle **1** (0.5 mmol), 0.5 mmol of alkynes **2**, 0.5 equiv of KOH in 2.0 mL of DMSO at 120 °C for 4 h. [b]1.5 equiv of KOH for 36 h. [c]0.5 equiv of KOH for 2 h. [d]1.5 equiv of KOH for 24 h.

After achieving the successful results with electron-donating alkynes, we next extend the scope of electron-withdrawing alkynes (**2r–v**), for the synthesis of (*E*)–addition products **5a-j** in good yields (Scheme 3). The reaction of **1a** with 1-ethynyl-4-(trifluoromethyl)benzene **2r** afforded the *E*–addition product **5a** in 65% yield. Cyano (**2s**) and flouro (**2t**) group containing aromatic terminal alkynes reacted in the same fashion to afford the (*E*)–selective

product **5b** and **5c** in good yields. It was interesting to note that the electron-deficient heteroaromatic alkyne **2u** also gave the corresponding product **5d** in 1 h. Furthermore, we examine the reactivity of aliphatic alkyne that is ethyl propiolate **2v** with **1a**. To our delight, the *E*–stereoselective product **5e** was obtained in 65% yield. The aza–carbazole **1h** reacted smoothly with alkyne **2r** to provide the *E*–isomer **5f** in moderate yield. Similarly, carbazole like 2, 3, 4, 9-tetrahydro-1*H*-carbazole **1j** reacted with alkyne **2r** and **2v** to give thermodynamically stable (*E*)-addition product **5g–h** in 62-70% yields, respectively. Other analogs like gamma–carboline **1i** provided the trans hydroaminated product **5i** and 2, 3, 4, 5-tetrahydro-1*H*-pyrido [4, 3-*b*]indole **1k** provided the bis-styrylated product **5j** in good yield. The above results indicated that the electron-withdrawing and electron-releasing group of alkynes plays an important role in controlling the regio- and stereoselectivity of the product.

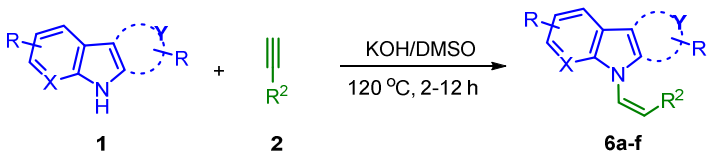
Scheme 3. Synthesis of Functionalized (*E*)–9-Styryl-9*H*-carbazoles analogs[a]



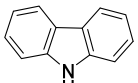
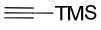
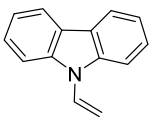
[a]The reactions were performed using *N*–heterocycles **1** (0.5 mmol), 0.5 mmol of alkynes **2**, 0.5 equiv of KOH in 2.0 mL of DMSO at 120 °C for 0.5 h. [b]0.25 h. [c]1 h.

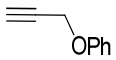
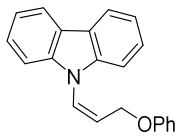
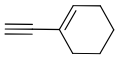
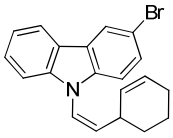
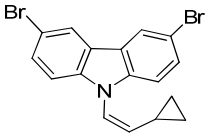
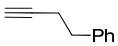
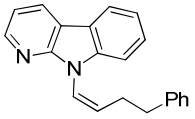
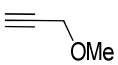
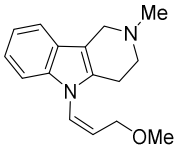
Encourage from the above nucleophilic addition of carbazoles, aza-carbazoles and gamma carbolines onto the aromatic terminal and internal alkynes, we intended to explore the reaction over aliphatic alkynes (Table 3). We synthesized a library of compounds **6a–f** in good yields. The reaction of ethynyltrimethylsilane **2aa** and carbazole **1a** using 0.5 equiv of KOH in DMSO at 120°C for 2 h, provided the addition product **6a** in 62% yield with the elimination of –TMS group (entry 1). Carbazole **1a** reacts smoothly with phenyl propargyl ether **2ba** to gave the desired product **6b** in 65% yield (entry 2). Interestingly, when 1-ethynylcyclohex-1-ene **2ca** was subjected towards the hydroamination reactions, the desired product was obtained in 64% yield (entry 3). Ethynylcyclopropane **2da** was found to be effective with substrate **1d** to afford the corresponding product **6d** in 60% yield (entry 4). Aza–carbazole **1h** and gamma carboline **1i** reacted incredibly with aliphatic alkynes. The reaction of 1-but-3-yn-1-ylbenzene **2ea** with **1h** afforded the hydroaminated product **6e** in 72% yield (entry 5). Addition of gamma–carboline **1i** onto methyl propargyl ether **2fa** provided the desired product **6f** in 65% yield (entry 6).

Table 3. Scope of Aliphatic Alkynes[a]



1 **2** **6a-f**

entry	carbazoles	alkyne **2**	product **6**	yield (%)
1	 **1a**		**2aa** 	**6a** 62

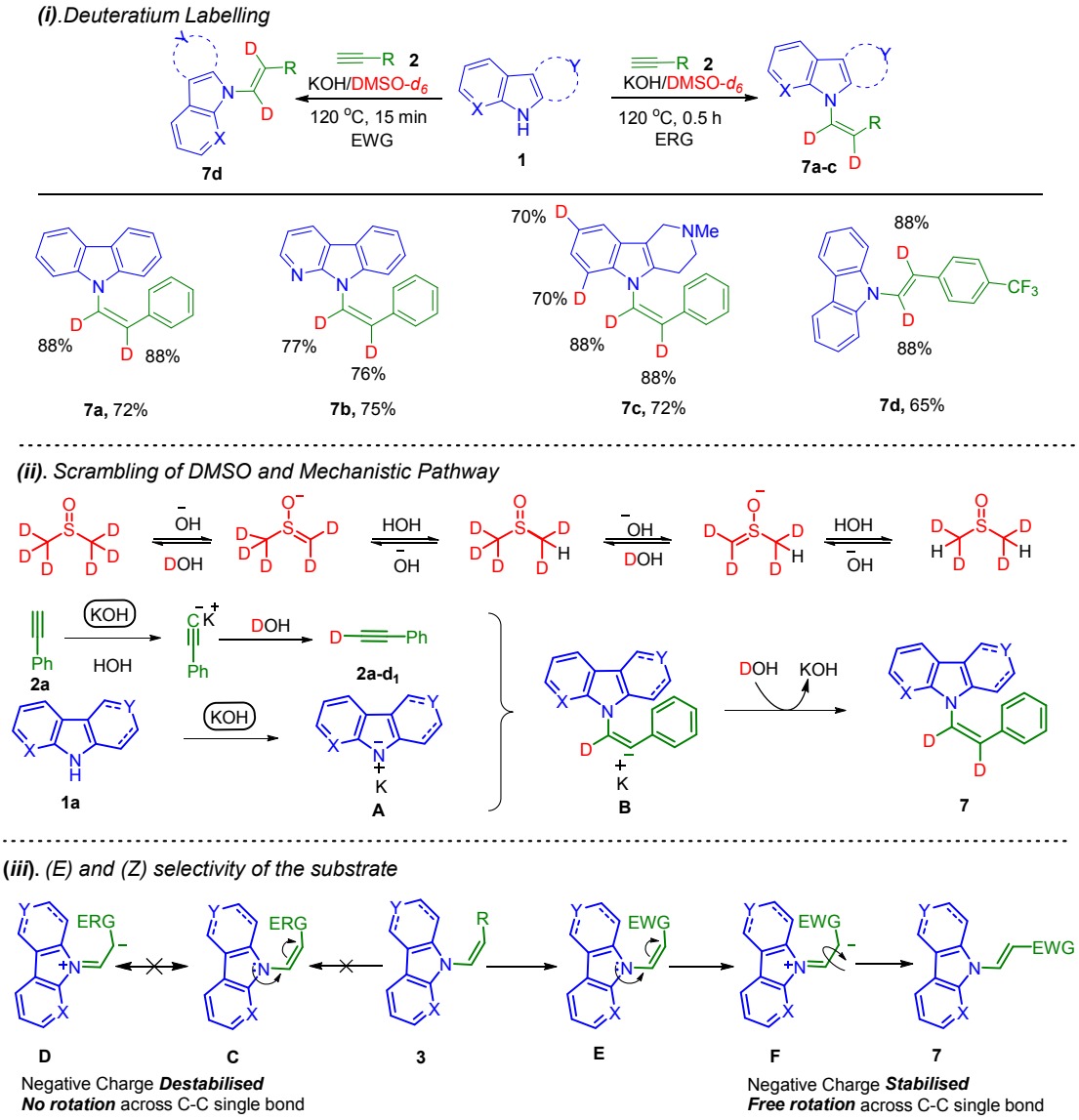
2	**1a**		**2ba**		**6b**	65
3	**1g**		**2ca**		**6c**	64
4	**1d**		**2da**		**6d**	60
5 [b]	**1h**		**2ea**		**6e**	72
6	**1i**		**2fa**		**6f**	65

[a]The reactions were performed using *N*–heterocycles **1** (0.5 mmol), 0.5 mmol of alkynes **2**, 0.5 equiv of KOH in 2.0 mL of DMSO at 120 °C for 2 h. [b]12 h.

In order to support the proposed mechanistic pathways several isotopic labelling experiments were conducted (Scheme 4, i-iii). The varieties of deuterated compounds **7a**–**d** were synthesized in good yields using KOH/DMSO–d_6 catalytic system (Scheme 4, i). The incorporation of deuterium at styryl position in compounds **7a**–**b** and **7d** reveal that the incoming protons were provided by the solvent. However, in the case of compound **7c**, the 70% H-D exchange occurred at C-6 and C-8 positions of the core moiety along with the styryl deuteration. This might be due to the high electron-density of the indole ring of gamma carboline **1i** as compared to carbazole **1a** and aza-carbazole **1h** (Figure 3 see ESI).[25] Based on the above evidence, the reaction pathway was proposed for the synthesis of *N*-styrylated

carbazole analogs (Scheme 4, ii). The reaction was initiated by the *in situ* formation of deuterated alkyne[27] **2a–d$_1$** from phenylacetylene by KOH/DOH which was present in the solution due to the scrambling of DMSO–d_6 in KOH.[25] Simultaneously, the anion of carbazole derivatives **A** was formed by abstraction the proton in super basic system. The attack of species **A** on alkyne **2a–d$_1$** in anti-markonikov fashion generate the species **B** which on subsequent deuteration forms the desired compound **7a–d**.

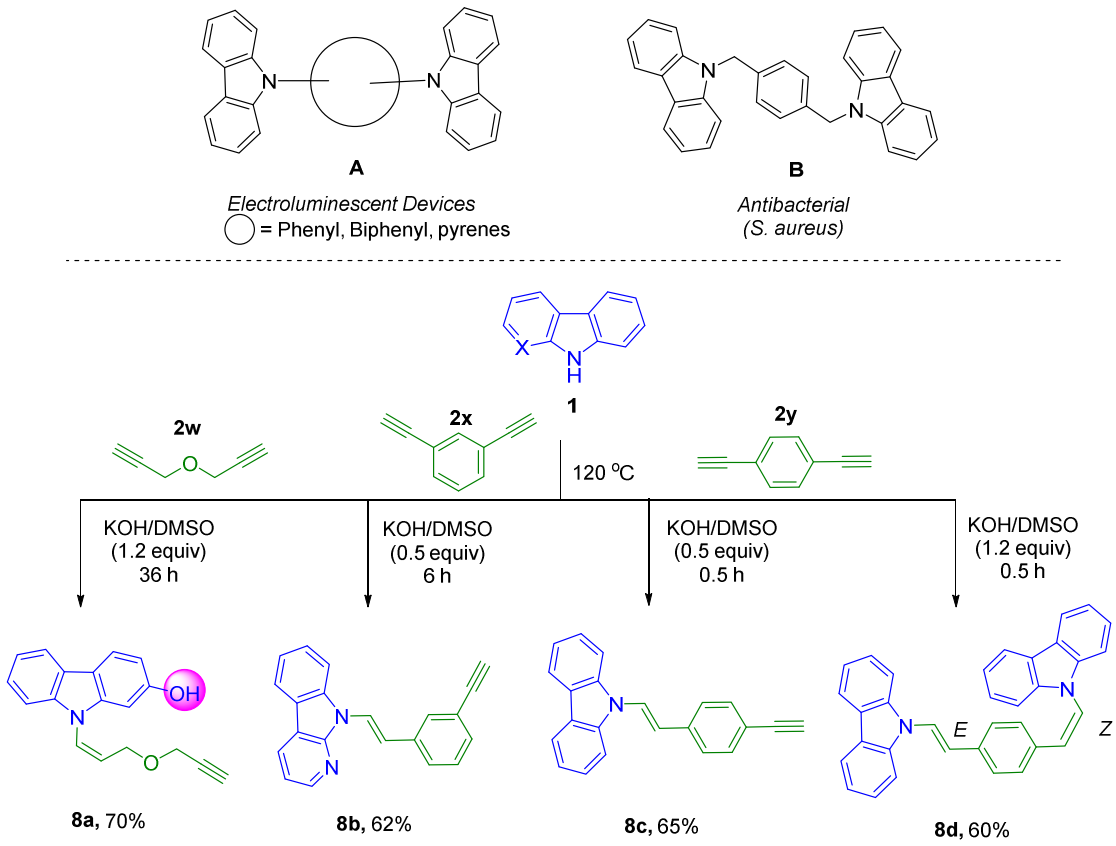
Scheme 4. Mechanistic Investigation



While investigating the substrate scope of the reaction, we found that the electronic effect of the alkynes influences the stereoselectivity of the product. This anomaly has been governed by the electron-donating and electron-withdrawing nature of the alkyne. After observing the substrate controlled behavior, we proposed the possible reason for their reactivity (Scheme 4, iii). In the case of electron-rich alkynes, the flow of electron was not feasible probably due to the electronic effect of the phenyl ring. Therefore, the benzyl anion species **D** was not formed. While in the case of electron-deficient alkynes the benzyl anion species **F** was stabilized by the electron-withdrawing group. Now, the species **F** is free to rotate across C-C single bond and formed the desired (*E*)–addition product. However, the rotation was not possible in case of species **C** probably due to the instability of benzylic anion.

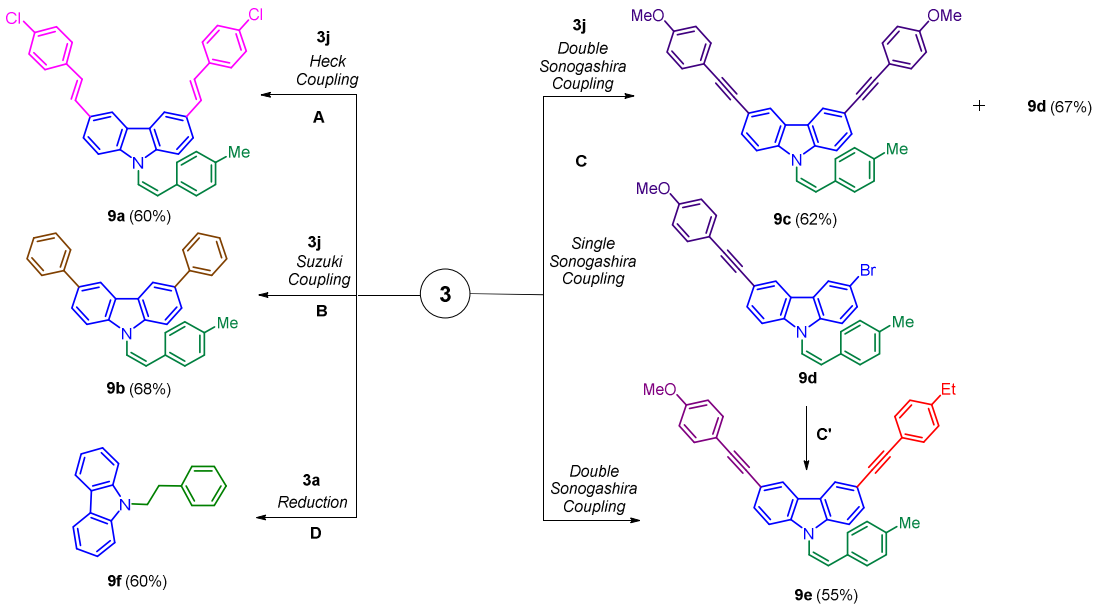
Bis-carbazolyl analogues bridged by phenyl, biphenyl and pyrenes as linker **A** are widely used as electroluminescent devices[28] and the compound **B** act as an antibacterial agent[29] which effectively inhibit the growth of *S. aureus*. We further explore the possibility of the reaction with dialkynes (Scheme 5). Inspired by the Marciniec *et.al* [22] protocol we endeavor to synthesized mono and di–styrylated carbazolyl compounds **8a–d** in a single step under metal-free environment by using KOH/DMSO at 120 ^{o}C for 0.5 h. An interesting observation was found when ether-linkage dialkyne **2w** was reacted with carbazole **1b**, the mono hydroaminated product **8a** was obtained in 70% yield. Aza–carbazole **1h** reacted smoothly with alkyne **2x** at 120 ^{o}C, for 6 h to provide the mono hydroaminated product **8b** in 62% yield. The reaction of 1,4-diethynylbenzene **2y** in the presence of **1a** using KOH (0.5 equiv) at 120 ^{o}C, for 0.5 h provided the (*E*)-9-(4-Ethynylstyryl)-9*H*-carbazole **8c** in 65% yield, however; when the reaction was carried out using KOH (1.2 equiv) at 120 ^{o}C, for 0.5 h, the desired product **8d** was obtained in 60% yield (Scheme 5).

Scheme 5. Synthesis of Mono and Bis–hydroaminated heterocycles



Regio– and stereoselective hydroamination of carbazoles provided the products **3j** which was further diversified by the palladium-catalyzed Sonogashira,[30a-b] Heck[30b-c] and Suzuki[30d-e] coupling reactions (Scheme 6). The synthesized carbazole **3j** was subjected towards the Heck coupling reactions using 1-chloro-4-vinylbenzene **10** and Suzuki cross-coupling in the presence of phenyl boronic acid **11** the coupling products **9a–b** was obtained in 60 and 68% yields, respectively. The C-C coupling of **3j** with alkyne **2z** gave a mixture of mono– **9d** and di–sonogashira **9c** coupled product. Further, the mono-sonogashira coupled product **9d** was converted into di-sonogashira product **9e** using alkyne **2n** as a coupling partner. The hydrogenation of **3a** using 10 mol % of Pd/C in EtOAc:MeOH (4:1)[30f] leads to the formation of reduced product 9-phenethyl-9*H*-carbazole **9f** in 60% yield.

Scheme 6. Synthetic Elaboration



(**A**) *Heck Coupling*: The reactions were performed using **3j** (1.0 equiv), 1-chloro-4-vinylbenzene **10** (10 equiv), $PdCl_2/PPh_3$ (10/30 mol%), Et_3N (10 equiv) in DMF at 100 °C for 24 h. (**B**) *Suzuki Coupling*: Compound **3j** (1.0 equiv), phenylboronic acid **11** (2.2 equiv), $PdCl_2/PPh_3$ (10/20 mol%), K_2CO_3 (6 equiv) in Dioxane:Water (1:1) at 100 °C for 2 h. (**C**) *Sonogashira Coupling*: Compound **3j** (1equiv), 1-ethynyl-4-methoxybenzene **2z** (2.0 equiv), $PdCl_2/PPh_3$ (10/20 mol%), Et_3N (3 equiv) in acetonitrile at 70 °C for 4 h. (**C'**) Compound **3j** (1equiv), 1-ethyl-4-ethynylbenzene **2n** (1.0 equiv), $PdCl_2/PPh_3$ (5/10 mol%), Et_3N (1.5 equiv) in acetonitrile at 70 °C for 2 h. (**D**) Compound **3a** with Pd/C (10 mol%), EtOAc:MeOH (4:1).

CONCLUSIONS

In conclusion, we reported the regio- and stereoselective hydroamination reaction of carbazoles, aza–carbazoles and γ–carbolines with electron-neutral, electron-rich and electron-deficient alkynes to yield a variety of (*Z*) and (*E*) styryl carbazoles derivatives. The protocol was driven through the electronic nature of the alkyne, electron–donating alkyne provided (*Z*)–stereoselective product and electron-withdrawing alkyne provided (*E*)–stereoselective products. The superbasic system of KOH/DMSO shows commendable results in case of aliphatic alkynes with tricyclic heterocycles. The reaction of 1,3 and 1,4 dialkynes with carbazoles provided a feasible route for the construction of mono– and bis– styrylated carbazoles. Synthesized

carbazoles were further synthetically elaborated by palladium–catalyzed cross coupling reaction and reduction reaction which increases the efficacy of the synthesized products. The deuterium-labeling experiments support the proposed mechanistic pathway.

EXPERIMENTAL SECTION

General Information and Method. All the reactions were performed in an oven-dried Schlenk flask under an argon atmosphere. Column chromatography was performed using silica gel (mesh 100-200). TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$. Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br s = broad singlet), coupling constants in Hertz, and integration. High–resolution mass spectra were recorded with q–TOF electrospray mass spectrometer. All purchased chemicals were used as received. All melting points are uncorrected.

General Procedure for the Synthesis of *N*-Styryl Cabazoles (3a–l and 3m–r) with Aromatic Terminal and Internal Alkynes: In an oven dried pressure tube, to a solution of carbazole **1a–f** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (0.5 equiv, 14 mg, 0.25 mmol) and alkynes **2a–h** (1.0 mmol), was added then, the resulting reaction mixture was heated at 120 °C for 0.5 h for the synthesis of products **3a-l**. Similarly for the synthesis of compounds **3m-r** we initiated the reaction with carbazole **1a–b** and **1g** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (1.5 equiv, 42 mg, 0.75 mmol) and alkynes **2i–m** (1.0 mmol), was added then, the resulting reaction mixtures was heated at 120 °C for 24 h. Progression of the reaction was monitored by TLC,

while noticing complete consumption of alkynes, reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel mesh size 100–200 (hexane).

(Z)-9-Styryl-9H-carbazole (***3a***). The product was obtained as a yellow solid (99.5 mg, 74% yield), mp: 90–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2H), 7.26 (t, J = 8.3 Hz, 3H), 7.19–7.12 (m, 4H), 7.03–7.01 (m, 2H), 6.94–6.91 (m, 2H), 6.74 (d, J = 9.1 Hz, 1H), 6.57 (d, J = 9.1 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.4, 131.7, 131.3, 128.7, 127.1, 125.9, 125.6, 125.2, 123.9, 121.2, 120.1, 111.1; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{16}N$ 270.1283; found 270.1263.

(Z)-9-(4-Butylstyryl)-9H-carbazole (***3b***). The product was obtained as a yellow needles (113.7 mg, 70% yield), mp: 89–91 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 11.4 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 9.1 Hz, 1H), 6.67 (d, J = 9.1 Hz, 1H), 2.51 (t, J = 7.3 Hz, 2H), 1.56–1.50 (m, 2H), 1.34–1.27 (m, 2H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 142.8, 139.3, 132.0, 128.7, 128.3, 126.7, 125.8, 123.9, 121.1, 120.11, 120.06, 111.1, 35.3, 33.2, 22.2, 13.9; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{24}H_{24}N$ 326.1909; found 326.1900.

(Z)-9-(3-Methoxystyryl)-9H-carbazole (***3c***). The product was obtained as a fluorescent yellow oil (104.6 mg, 70% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.40–7.35 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 7.07–7.03 (m, 1H), 6.95 (d, J = 10.6 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.70–6.65 (m, 1H), 6.66 (d, J = 8.3 Hz, 1H), 6.54 (s, 1H), 3.32 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.2, 139.1, 135.8, 129.1, 126.2, 125.9, 123.8, 122.0,

121.6, 120.2, 120.1, 114.4, 113.3, 111.1, 54.7; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; found 300.1388.

(Z)-3-(2-(9H-Carbazol-9-yl)vinyl)aniline (***3d***). The product was obtained as a brown needles (96.5 mg, 68% yield), mp: 130–132 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 6.8 Hz, 2H), 7.38–7.34 (m, 3H), 7.27 (s, 1H), 7.23–7.20 (m, 3H), 6.91–6.86 (m, 3H), 6.57 (d, J = 8.3 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 6.46 (d, J = 6.8 Hz, 1H), 6.40 (br s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 146.1, 139.3, 135.7, 129.1, 126.4, 125.9, 123.9, 121.8, 120.2, 120.0, 119.5, 115.2, 114.8, 111.2; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{17}N_2$ 285.1392; found 285.1405.

(Z)-4-(2-(9H-Carbazol-9-yl)vinyl)-N,N-dimethylaniline (***3e***). The product was obtained as a brown needles (107.6 mg, 69% yield), mp: 85–87 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.38–7.34 (m, 2H), 7.28–7.23 (m, 4H), 6.93 (d, J = 8.3 Hz, 2H), 6.66 –6.58 (m, 2H), 6.40 (d, J = 9.1 Hz, 2H), 2.84 (s, 6H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 150.1, 139.6, 132.3, 130.1, 127.9, 125.8, 123.7, 120.0, 119.8, 117.9, 111.7, 111.1, 40.1; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{22}H_{21}N_2$ 313.1705; found 313.1725.

(Z)-9-(2-(Thiophen-3-yl)vinyl)-9H-carbazole (***3f***). The product was obtained as a off white needles (89.3 mg, 65% yield), mp: 128–130 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.37–7.33 (m, 2H), 7.28–7.20 (m, 4H), 6.99 (s, 1H), 6.97–6.94 (m, 1H), 6.78–6.73 (m, 2H), 6.58–6.56 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.5, 135.5, 127.8, 125.9, 125.8, 125.6, 125.2, 123.8, 122.3, 120.7, 120.2, 110.9; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{18}H_{14}NS$ 276.0847; found 276.0843.

9-(3-Methoxystyryl)-9H-carbazol-2-ol (***3g***). The product was obtained as a brown needles (110.2 mg, 70% yield), mp: 126–128 °C, ^{1}H NMR (400 MHz, $CDCl_3$) (stereoisomers *E*:*Z* :: 60:40) δ 7.96 (d, J = 7.6 Hz, 2.01 H), 7.90–7.87 (m, 2 H), 7.64 (d, J = 7.6 Hz, 0.78 H), 7.58 (d, J = 14.5

Hz, 1.0 H major regioisomer), 7.41 (t, *J* = 7.6 Hz, 0.86 H), 7.32–7.27 (m, 2.99 H), 7.25–7.22 (m, 1.6 H), 7.16–7.14 (m, 2.05 H), 7.09–7.05 (m, 1.2 H), 7.03–7.01 (m, 2.04 H), 6.95 (d, *J* = 14.5 Hz, 1.0 H), 6.87–6.84 (m, 0.8 H), 6.83–6.76 (m, 3.24 H), 6.72–6.68 (m, 2.37 H), 6.629–6.623 (m, 1.08 H), 6.56 (d, *J* = 9.1 Hz, 1.3H minor regioisomer), 6.54–6.53 (m, 1.53 H), 5.85 (br s, 1.66 H), 3.86 (s, 2.4 H), 3.33 (s, 3.04 H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) (stereoisomers *E*:*Z* :: 60:40) δ 159.8, 159.1, 155.1, 154.8, 140.8, 140.5, 139.6, 139.2, 137.6, 135.8, 129.8, 129.2, 126.3, 125.0, 124.6, 124.2, 123.9, 123.4, 121.9, 121.7, 121.1, 121.0, 120.8, 120.3, 119.3, 119.2, 118.4, 117.9, 117.6, 114.3, 113.7, 112.6, 111.3, 110.9, 110.3, 109.6, 109.2, 97.6, 97.3, 55.3, 54.7; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{18}NO_2$ 316.1338; found 316.1341.

(Z)-2-Methoxy-9-styryl-9H-carbazole (***3h***). The product was obtained as a brown semi–solid (107.6 mg, 72% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.88 (m, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.17–7.15 (m, 1H), 7.13–7.11 (m, 1H), 7.04–7.00 (m, 5H), 6.84–6.82 (m, 1H), 6.76 (dd, *J* = 8.7 and 1.5 Hz, 1H), 6.56 (d, *J* = 9.1 Hz, 1H), 6.48–6.47 (m, 1H), 3.65 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 158.9, 140.3, 139.4, 135.0, 128.9, 128.7, 128.3, 127.8, 125.9, 125.7, 124.6, 122.1, 120.7, 120.4, 119.2, 110.7, 109.3, 95.4, 55.4; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; found 300.1388.

(Z)-3,6-Dibromo-9-styryl-9H-carbazole (***3i***). The product was obtained as a light yellow needles (146.2 mg, 69% yield), mp: 154–156°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.17 (m, 2H), 7.67–7.58 (m, 1H), 7.53–7.50 (m, 2H), 7.24–7.17 (m, 2H), 7.13 (d, *J* = 9.9 Hz, 2H), 7.08–7.06 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 138.0, 134.1, 129.2, 128.5, 128.4, 128.2, 127.6, 124.3, 123.0, 120.8, 113.4, 112.5; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{14}Br_2N$ 425.9493; found 425.9493.

(Z)-3,6-Dibromo-9-(4-methylstyryl)-9H-carbazole (***3j***). The product was obtained as a white needles (155.4 mg, 71% yield), mp: 161–163 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.108–8.104 (m, 2H), 7.42 (dd, J = 10.6 and 2.2 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 6.90–6.83 (m, 4H), 6.73 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 9.1 Hz, 1H), 2.21 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 138.3, 138.1, 131.2, 129.3, 129.2, 128.6, 128.1, 124.3, 123.1, 120.0, 113.4, 112.6, 21.2; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{16}Br_2N$ 439.9649; found 439.9641.

(Z)-9-(4-(tert-Butyl)styryl)-9H-carbazole-3-carbonitrile (***3k***). The product was obtained as a yellow oil (119.0 mg, 68% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.55 (dd, J = 8.3 and 1.5 Hz, 1H), 7.49–7.47 (m, 1H), 7.45–7.41 (m, 2H), 7.20 (d, J = 9.1 Hz, 1H), 7.11 (d, J = 8.3 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 6.83–6.76 (m, 2H), 1.19 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 151.8, 140.9, 140.2, 130.9, 130.0, 129.3, 129.1, 128.5, 127.4, 125.9, 125.5, 125.0, 122.6, 121.4, 120.6, 119.8, 111.7, 111.3, 102.9, 34.6, 31.0; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{25}H_{23}N_2$ 351.1861; found 351.1856.

(Z)-9-(2-(Thiophen-3-yl)vinyl)-9H-carbazole-3,6-dicarbonitrile (***3l***). The product was obtained as a brown needles (105.6 mg, 65% yield), mp: 158–160 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.72 (m, 1H), 7.62–7.60 (m, 1H), 7.38–7.37 (m, 2H), 7.11–7.10 (m, 1H), 6.96–6.92 (m, 2H), 6.65 (d, J = 11.4 Hz, 1H), 6.13–6.09 (m, 2H), 5.72 (d, J = 11.4 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 141.8, 139.2, 133.7, 129.1, 128.8, 127.2, 126.7, 126.6, 125.6, 124.5, 120.9, 118.6, 111.5; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{12}N_3S$ 326.0752; found 326.0754.

(Z)-9-(1,2-Diphenylvinyl)-9H-carbazole (***3m***). The product was obtained as a off white needles (120.7 mg, 70% yield), mp: 149–151 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 7.34 (s, 1H), 7.33–7.20 (m, 9H), 7.07–7.03 (m, 2H), 7.02–6.96 (m, 3H), 6.86–6.84 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.5, 137.7, 134.7, 133.7, 131.6, 128.74, 128.68, 128.5,

128.4, 128.0, 127.4, 126.0, 125.9, 123.6, 120.2, 119.9, 111.1; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{26}H_{20}N$ 346.1596; found 346.1604.

(Z)-9-(1-Phenylprop-1-en-2-yl)-9H-carbazole (***3n***). The product was obtained as a pale yellow needles (99.0 mg, 70% yield), mp: 120–122 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 2H), 7.52–7.47 (m, 4H), 7.46–7.42 (m, 2H), 7.35 (t, J = 6.8 Hz, 2H), 7.29–7.25 (m, 1H), 7.25 (s, 2H), 6.87 (s, 1H), 2.39 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 140.2, 135.7, 133.3, 131.6, 130.6, 129.0, 128.5, 127.5, 125.8, 123.2, 120.3, 119.5, 109.9, 17.5; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{18}N$ 284.1439; found 284.1415.

(Z)-9-(2-(2-Bromophenyl)-1-(4-methoxyphenyl)vinyl)-9H-carbazole (***3o***). The product was obtained as a white needles (154.0 mg, 68% yield), mp: 180–182 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.49–7.47 (m, 1H), 7.33–7.32 (m, 1H), 7.27–7.19 (m, 6H), 7.06 (d, J = 8.3 Hz, 2H), 6.83–6.79 (m, 3H), 6.61–6.57 (m, 1H), 6.46 (d, J = 10.6 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 160.4, 139.9, 135.5, 132.4, 129.6, 128.8, 128.3, 127.8, 127.1, 125.9, 124.3, 124.0, 123.5, 120.0, 119.9, 114.2, 111.1, 55.3; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{21}BrNO$ 454.0807; found 454.0807.

(Z)-9-(2-(4-Nitrophenyl)-1-(thiophen-3-yl)vinyl)-9H-carbazole (***3p***). The product was obtained as a straw yellow needles (132.6 mg, 67% yield), mp: 126–128 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.14 (m, 2H), 7.83–7.81 (m, 2H), 7.34 (s, 1H), 7.33–7.31 (m, 1H), 7.29–7.26 (m, 4H), 7.22–7.20 (m, 1H), 7.08–7.06 (m, 2H), 6.93 (s, 1H), 6.91–6.90 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 146.3, 141.0, 139.03, 138.98, 133.3, 128.8, 127.1, 126.2, 125.2, 124.8, 123.70, 123.66, 123.5, 120.5, 120.4, 110.7; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{24}H_{17}N_2O_2S$ 397.1011; found 397.1004.

(Z)-9-(1,2-Diphenylvinyl)-9H-carbazol-2-ol (***3q***). The product was obtained as a yellow needles (111.9 mg, 62% yield), mp: 135–138 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.93 (m, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.26 (s, 1H), 7.21–7.18 (m, 2H), 7.15–7.14 (m, 3H), 7.14–7.11 (m, 3H), 6.98–6.91 (m, 3H), 6.82–6.80 (m, 3H), 6.67 (dd, J = 10.8 and 2.2 Hz, 1H), 6.42 (d, J = 2.2 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 154.7, 141.0, 139.6, 137.5, 134.6, 128.8, 128.7, 128.5, 128.4, 128.1, 127.5, 125.9, 124.8, 121.1, 120.0, 119.3, 110.8, 109.1, 97.2; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{26}H_{20}NO$ 362.1545; found 362.1547.

(Z)-9-(1,2-bis(3-Methoxyphenyl)vinyl)-3-bromo-9H-carbazole (***3r***). The product was obtained as a orange needles (156.9 mg, 65% yield), mp: 142–143 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.148–8.146 (m, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.26–7.25 (m, 1H), 7.20 (d, J = 8.3 Hz, 1H), 7.16 (d, J = 6.8 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 8.3 Hz, 2H), 6.79–6.76 (m, 1H), 6.73 (s, 1H), 6.70 (d, J = 8.3 Hz, 1H), 6.52 (dd, J = 8.3 and 1.5 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H), 6.08 (s, 1H), 3.63 (s, 3H), 3.10 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 160.0, 159.3, 139.9, 138.9, 138.2, 135.5, 133.2, 129.9, 129.3, 128.7, 127.8, 126.8, 125.2, 122.9, 122.4, 121.7, 120.4, 120.3, 118.4, 115.2, 114.0, 112.9, 112.4, 112.1, 111.7, 111.2, 55.2, 54.5; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{28}H_{23}BrNO_2$ 484.0912; found 484.0912.

General Procedure for the Synthesis of *N*–Styryl Aza-cabazoles (4a–e) and *N*–Styryl γ–Carbolines with Aromatic Alkynes (4f–l): In an oven dried pressure tube, to a solution of aza-cabazole **1i** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (0.5 equiv, 14mg, 0.25 mmol) and alkynes **2** (0.5 mmol) were added then, the resulting reaction mixture was heated at 120 °C for 4 h for the synthesis of products **4a**–**e**. Similarly, for the synthesis of compounds **4f**–**l** we initiated the reaction with γ–carboline **1j** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (0.5 equiv, 14mg, 0.25 mmol) and alkynes **2** (0.5 mmol), the resulting reaction mixtures was

heated at 120 °C for 2 h. Progression of the reaction was monitored by TLC, while noticing complete consumption of alkynes, reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel mesh size 100–200 (hexane).

(Z)-9-Styryl-9H-pyrido[2,3-b]indole (***4a***). The product was obtained as a light brown needles (105.3 mg, 78% yield), mp: 132–134 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50–8.49 (m, 1H), 8.33 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 6.8 Hz, 1H), 7.29–7.22 (m, 3H), 7.15 (d, J = 9.1 Hz, 1H), 7.10–7.04 (m, 5H), 6.99 (d, J = 8.3 Hz, 1H), 6.76 (d, J = 9.1 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 151.6, 146.4, 137.5, 134.9, 128.7, 128.19, 128.15, 127.8, 126.8, 126.7, 121.4, 121.0, 120.7, 116.9, 116.3, 112.2; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{19}H_{15}N_2$ 271.1235; found 271.1207.

(Z)-9-(4-Ethylstyryl)-9H-pyrido[2,3-b]indole (***4b***). The product was obtained as a brown needles (111.7 mg, 75% yield), mp: 120–122 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 5.3 and 1.5 Hz, 1H), 8.26 (dd, J = 7.6 and 1.5 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.55–7.52 (m, 1H), 7.17–7.14 (m, 2H), 7.00 (d, J = 9.1 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.90–6.82 (m, 4H), 6.67 (d, J = 9.1 Hz, 1H), 2.43 (q, J = 7.6 Hz, 2H), 1.04 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 151.6, 146.4, 144.0, 137.7, 132.1, 130.1, 128.8, 127.7, 127.3, 126.7, 125.9, 121.4, 120.7, 120.1, 116.8, 116.2, 112.3, 28.5, 15.2; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{19}N_2$ 299.1548; found 299.1562.

(Z)-9-(3-Methoxystyryl)-9H-pyrido[2,3-b]indole (***4c***). The product was obtained as a brown semi–solid (105.0 mg, 70% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.42 (m, 1H), 8.26 (d, J

= 7.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.24–7.20 (m, 1H), 7.18–7.15 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.95–6.91 (m, 2H), 6.67 (d, *J* = 9.1 Hz, 1H), 6.62–6.58 (m, 2H), 6.44 (s, 1H), 3.25 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 159.2, 151.6, 146.4, 137.6, 136.0, 129.1, 128.2, 126.8, 126.7, 121.6, 121.3, 121.1, 120.8, 120.7, 116.8, 116.3, 114.3, 113.3, 112.3, 54.7; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{17}N_2O$ 301.1341; found 301.1342.

(Z)-9-(2-(Thiophen-3-yl)vinyl)-9H-pyrido[2,3-b]indole (***4d***). The product was obtained as a off–white needles (99.3 mg, 72% yield), mp: 126–128 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.41 (m, 1H), 8.27 (dd, *J* = 7.6 and 1.5 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.30–7.27 (m, 1H), 7.22–7.20 (m, 1H), 7.18–7.14 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.93–6.89 (m, 2H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.48–6.46 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 151.7, 146.5, 138.1, 135.5, 128.2, 127.7, 126.8, 125.7, 125.1, 122.9, 121.3, 120.83, 120.78, 119.7, 116.7, 116.2, 111.9; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{17}H_{13}N_2S$ 277.0799; found 277.0800.

(*Z)-9-(1,2-Diphenylvinyl)-9H-pyrido[2,3-b]indole* (***4e***). The product was obtained as a light yellow needles (121.0 mg, 70% yield), mp: 145–147 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31–8.28 (m, 2H), 8.05 (d, *J* = 6.8 Hz, 1H), 7.44 (s, 1H), 7.26 (t, *J* = 8.3 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.18–7.16 (m, 5H), 7.10–7.07 (m, 2H), 6.94–6.87 (m, 3H), 6.80–6.79 (m, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 151.4, 146.9, 138.9, 137.6, 134.8, 132.6, 128.7, 128.5, 128.4, 128.30, 128.25, 127.9, 127.1, 125.6, 121.0, 120.9, 120.7, 116.5, 115.9, 111.2; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{25}H_{19}N_2$ 347.1548; found 347.1520.

(Z)-2-Methyl-5-styryl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4f***). The product was obtained as a brown needles (108.0 mg, 75% yield), mp: 140–142 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.26–7.24 (m, 1H), 7.15–7.12 (m, 2H), 7.11–7.09 (m,

2H), 7.00–6.98 (m, 2H), 6.73 (d, J = 9.1 Hz, 1H), 6.52 (d, J = 8.7 Hz, 1H), 3.73–3.72 (m, 2H), 2.73–2.70 (m, 2H), 2.60–2.57 (m, 2H), 2.53 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 136.3, 135.6, 134.7, 133.0, 128.8, 128.5, 128.4, 127.9, 127.0, 125.7, 122.3, 119.9, 117.4, 110.8, 52.4, 51.6, 45.5, 23.2; HRMS (EI$^-$TOF) *m/z*: $(M)^+$ Calcd for $C_{20}H_{20}N_2$ 288.1626; found 288.1625.

(Z)-5-(4-(tert-Butyl)styryl)-2-methyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4g***). The product was obtained as a brown semi–solid (120.4 mg, 70% yield), ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 1H), 7.08–7.05 (m, 3H), 7.04–7.00 (m, 2H), 6.86 (d, J = 8.3 Hz, 2H), 6.57 (d, J = 8.3 Hz, 1H), 6.43 (d, J = 8.3 Hz, 1H), 3.65 (s, 2H), 2.65–2.63 (m, 2H), 2.55–2.52 (m, 2H), 2.45 (s, 3H), 1.15 (s, 9H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 151.1, 135.8, 133.3, 131.6, 128.4, 127.8, 126.4, 125.4, 121.5, 121.3, 119.8, 117.4, 110.8, 110.7, 52.4, 51.7, 45.6, 34.5, 31.1, 23.2; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{24}H_{29}N_2$ 345.2331; found 345.2351.

(Z)-2-Methyl-5-(4-(trifluoromethoxy)styryl)-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4h***). The product was obtained as a yellow semi–solid (133.9 mg, 72% yield), ^1H NMR (400 MHz, DMSO-d_6) δ 7.83–7.81 (m, 1H), 7.77–7.72 (m, 1H), 7.41–7.37 (m, 1H), 7.33 (d, J = 9.1 Hz, 1H), 7.16–7.12 (m, 2H), 7.03–6.99 (m, 3H), 6.67 (d, J = 9.6 Hz, 1H), 3.54 (s, 2H), 2.61–2.58 (m, 2H), 2.43 (s, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6) δ 147.3, 134.6, 134.0, 133.1, 129.9, 127.3, 126.0, 124.5, 123.5, 121.1, 120.8, 119.8, 117.5, 111.4, 110.5, 51.7, 51.0, 45.1, 22.8; HRMS (EI$^-$TOF) *m/z*: $(M)^+$ Calcd for $C_{21}H_{19}F_3N_2O$ 372.1444; found 372.1450.

(Z)-2-Methyl-5-(2-(thiophen-2-yl)vinyl)-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4i***). The product was obtained as a brown semi–solid (105.8 mg, 72% yield), ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 1H), 7.13–7.09 (m, 3H), 7.03–7.01 (m, 1H), 6.96–6.95 (m, 1H), 6.64–6.58 (m, 2H), 6.50–6.49 (m, 1H), 3.73 (s, 2H), 2.76–2.73 (m, 2H), 2.65–2.63 (m, 2H), 2.54 (s, 3H);

$^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 135.7, 135.4, 132.2, 127.3, 126.2, 125.4, 125.2, 123.1, 121.3, 120.9, 119.8, 117.4, 110.5, 110.0, 52.4, 51.6, 45.5, 23.1; HRMS (EI-TOF) *m/z*: $(M)^+$ Calcd for $C_{18}H_{18}N_2S$ 294.1191; found 294.1192.

(Z)-5-(1,2-Di-p-tolylvinyl)-2-methyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4j***). The product was obtained as a brown semi–solid (137.2 mg, 70% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.35–7.33 (m, 2H), 7.31 (s, 1H), 7.24–7.20 (m, 2H), 7.15–7.11 (m, 4H), 7.09–7.05 (m, 1H), 6.96–6.92 (m, 2H), 2.51 (s, 2H), 2.39–2.37 (m, 2H), 2.34 (s, 6H), 2.29 (s, 3H), 2.14–2.11 (m, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 138.0, 136.0, 134.8, 132.1, 129.8, 129.4, 129.1, 128.6, 128.4, 128.2, 126.6, 126.1, 123.1, 123.0, 121.4, 119.6, 117.4, 111.1, 52.3, 51.6, 45.4, 29.7, 21.2; HRMS (EI-TOF) *m/z*: $(M)^+$ Calcd for $C_{28}H_{28}N_2$ 392.2252; found 392.2251.

(Z)-2-Methyl-5-(2-(4-nitrophenyl)-1-phenylvinyl)-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4k***). The product was obtained as a orange needles (126.7 mg, 62% yield), mp: 142–144 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, J = 9.1 Hz, 2H), 7.59 (s, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.35–7.34 (m, 3H), 7.17–7.14 (m, 2H), 7.01–6.97 (m, 3H), 6.92–6.88 (m, 1H), 6.77 (d, J = 9.1 Hz, 1H), 2.94 (s, 2H), 2.55–2.51 (m, 2H), 2.44 (s, 3H) 2.33 (s, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 146.0, 141.2, 137.8, 137.2, 135.3, 132.3, 129.4, 128.7, 128.6, 126.2, 125.9, 123.5, 121.6, 120.0, 117.5, 111.0, 110.6, 51.9, 51.2, 45.2, 22.8; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{26}H_{24}N_3O_2$ 410.1869; found 410.1886.

(Z)-2-Methyl-5-(2-(4-nitrophenyl)-1-(thiophen-3-yl)vinyl)-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***4l***). The product was obtained as a brown semi–solid (143.1 mg, 69% yield), ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, J = 8.7 Hz, 2H), 7.59–7.56 (m, 2H), 7.44 (d, J = 7.3 Hz, 1H),

7.28–7.26 (m, 1H), 7.00–6.97 (m, 2H), 6.93 (d, *J* = 9.1 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 3.63–3.58 (m, 2H), 2.57–2.51 (m, 2H), 2.44–2.43(m, 2H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, DMSO-d_6) δ 146.1, 141.5, 140.0, 135.2, 133.0, 132.9, 129.0, 128.1, 126.0, 125.5, 124.8, 123.9, 123.8, 121.8, 120.1, 118.1, 110.8, 110.3, 51.7, 51.1, 45.2, 22.6; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{24}H_{22}N_3O_2S$ 416.1433; found 416.1451.

General Procedure for the Synthesis of (*E*)–Styryl Carbazole/Aza-carbazole/γ–carbolines (5a–j): In an oven dried pressure tube, to a solution of carbazole/aza-carbazole/γ–carbolines **1** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (0.5 equiv, 14mg, 0.25 mmol) and alkynes **2r–v** (0.5 mmol) were added. The resulting reaction mixture was heated at 120 °C for 0.25 h - 0.5 h. Progression of the reaction was monitored by TLC, while noticing complete consumption of alkynes, reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel mesh size 100–200 (hexane).

(E)-9-(4-(Trifluoromethyl)styryl)-9H-carbazole (***5a***). The product was obtained as a pale yellow needles (109.5 mg, 65% yield), mp: 90–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 14.5 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.64–7.56 (m, 3H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.35–7.30 (m, 2H), 7.28–7.26 (m, 1H), 7.16–7.10 (m, 1H), 7.05–7.01 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 139.3, 128.8, 126.5, 126.1, 125.7 (q, *J* = 3.8 Hz, 1C), 125.7 , 125.3, 124.4, 121.3, 120.7, 120.4, 116.7, 110.7; HRMS (EI–TOF) *m/z*: $(M)^+$ Calcd for $C_{21}H_{14}F_3N$ 337.1078; found 337.1071.

(E)-4-(2-(9H-Carbazol-9-yl)vinyl)benzonitrile (***5b***). The product was obtained as a brown needles (95.5 mg, 65% yield), mp: 102–104 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 14.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.15 (d, J = 8.2 Hz, 1H), 7.12–7.08 (m, 1H), 7.04 (d, J = 14.6 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.2, 133.4 132.7, 132.3, 126.6, 126.4, 126.1, 125.9, 124.6, 121.6, 120.5, 120.4, 110.8. HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{15}N_2$ 295.1235; found 295.1249.

(E)-9-(2-Fluorostyryl)-9H-carbazole (***5c***). The product was obtained as a yellow liquid (88.9 mg, 62% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.7 Hz, 2H), 7.84 (d, J = 14.6 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.59–7.55 (m, 1H), 7.52–7.47 (m, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.25–7.23 (m, 1H), 7.20–7.18 (m, 1H), 7.16–7.12 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 160.0 (d, J = 248.2 Hz, 1C), 139.4, 128.3, 128.2, 126.9 (d, J = 3.8 Hz, 1C), 126.4, 125.9, 125.5 (d, J = 6.7 Hz, 1C), 124.40, 124.36, 124.2, 121.0, 120.3, 115.9 (d, J = 22.0 Hz, 1C), 111.6, 111.5, 111.95, 111.92, 110.6; ^{19}F NMR (400 MHz, $CDCl_3$) -114.24. HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{15}FN$ 288.1189; found 288.1180.

(E)-9-(2-(Pyridin-2-yl)vinyl)-9H-carbazole (***5d***). The product was obtained as a light yellow needles (86.4 mg, 64% yield), mp: 103–105 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51–8.50 (m, 1H), 8.40 (d, J = 14.2 Hz, 1H), 7.97 (d, J = 7.7 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.56–7.52 (m, 1H), 7.42–7.38 (m, 2H), 7.25–7.19 (m, 2H), 7.17–7.14 (m, 1H), 7.04–7.01 (m, 1H), 6.95 (d, J = 14.2 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 155.3, 149.9, 139.4, 136.9, 127.7, 126.9, 126.4, 124.5, 121.5, 120.6, 119.9, 115.2, 111.5. HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{19}H_{15}N_2$ 271.1235; found 271.1264.

Ethyl (E)-3-(9H-carbazol-9-yl)acrylate (***5e***). The product was obtained as a off-white solid (86.1 mg, 65% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 14.2 Hz, 1H), 8.03 (d, J = 7.7 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.52–7.48 (m, 2H), 7.38–7.34 (m, 2H), 6.32 (d, J = 14.2 Hz, 1H), 4.32 (q, J = 7.3 Hz, 2H), 1.38 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 168.1, 139.1, 137.5, 127.0, 125.5, 122.6, 120.4, 111.8, 101.5, 60.4, 14.1. HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{17}H_{16}NO_2$ 266.1181; found 266.1180.

(E)-9-(4-(Trifluoromethyl)styryl)-9H-pyrido[2,3-b]indole (***5f***). The product was obtained as a light yellow needles (118.3 mg, 70% yield), mp: 96–98 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50–8.48 (m, 1H), 8.26 (dd, J = 7.6 and 1.5 Hz, 1H), 8.09 (d, J = 14.5 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 15.2 Hz, 1H), 7.59–7.50 (m, 5H), 7.31 (t, J = 7.6 Hz, 1H), 7.23–7.20 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 146.3, 140.7, 138.2, 128.3, 128.2, 128.1, 127.5, 125.8, 125.6 (q, J = 3.8 Hz, 1C), 124.0, 121.8, 121.1, 117.3, 117.1, 115.8, 111.0; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{14}F_3N_2$ 339.1109; found 339.1103.

(E)-2-Methyl-5-(4-(trifluoromethyl)styryl)-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***5g***). The product was obtained as a pale yellow needles (119.3 mg, 70% yield), mp: 135–137 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, J = 16.4 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 7.9 Hz, 2H), 7.67 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 10.4 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H), 7.14–7.10 (m, 1H), 6.90 (d, J = 14.6 Hz, 1H), 3.53 (s, 2H), 3.02 (s, 2H), 2.74–2.71 (m, 2H), 2.42 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 140.9, 135.4, 133.4, 128.7, 126.5, 126.2, 126.1, 125.3 (q, J = 3.8 Hz, 1C), 123.1, 122.1, 120.8, 117.6, 113.8, 111.9, 111.5, 52.1, 51.0, 45.3, 24.0; HRMS (EI–TOF) *m/z*: $(M)^+$ Calcd for $C_{21}H_{19}F_3N_2$ 356.1500; found 356.1501.

(E)-9-(4-(Trifluoromethyl)styryl)-2,3,4,9-tetrahydro-1H-carbazole (***5h***). The product was obtained as a light yellow needles (83.3 mg, 62% yield), mp: 100–102 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 1H), 7.64–7.62 (m, 2H), 7.56 (d, J = 14.5 Hz, 1H), 7.52–7.49 (m, 3H), 7.29 (t, J = 7.6 Hz, 1H), 7.25–7.22 (m, 1H), 6.78 (d, J = 14.5 Hz, 1H), 2.87–2.84 (m, 2H), 2.78–2.75 (m, 2H), 2.03–1.97 (m, 2H), 1.94–1.85 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 140.5, 135.5, 135.0, 129.0, 128.6, 128.4, 128.0, 125.6 (q, J = 4.7 Hz, 1C), 125.4, 122.2, 120.9, 118.1, 114.3, 113.7, 110.9, 23.4, 23.2, 22.5, 20.9; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{19}F_3N$ 342.1470; found 342.1464.

(E)-Ethyl 3-(3,4-dihydro-1H-carbazol-9(2H)-yl)acrylate (***5i***). The product was obtained as a light yellow liquid (110.3 mg, 62% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 14.5 Hz, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.24–7.20 (m, 2H), 6.11 (d, J = 14.5 Hz, 1H), 4.34–4.28 (m, 2H), 2.83 (t, J = 5.3 Hz, 2H), 2.69 (t, J = 6.1 Hz, 2H), 1.96–1.95 (m, 2H), 1.88–1.87 (m, 2H), 1.38 (t, J = 6.1 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 168.2, 137.5, 128.1, 127.6, 125.6, 123.0, 122.2, 118.2, 116.3, 111.8, 100.2, 60.1, 23.0, 22.6, 22.2, 20.8, 14.0; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{17}H_{20}NO_2$ 270.1494; found 270.1494.

Diethyl 3,3'-(3,4-dihydro-1H-pyrido[4,3-b]indole-2,5-diyl)(2E,2'E)-diacrylate (***5j***). The product was obtained as a orange semi-solid (119.6 mg, 65% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.09 (m, 1H), 7.65–7.61 (m, 2H), 7.40 (d, J = 7.7 Hz, 1H), 7.32 (t, J = 8.2 Hz, 1H), 7.27–7.25 (m, 1H), 6.05 (d, J = 14.2 Hz, 1H), 4.86 (d, J = 12.8 Hz, 1H), 4.35 (s, 2H), 4.27 (q, J = 7.3 Hz, 2H), 4.16 (q, J = 7.3 Hz, 2H), 3.66 (t, J = 5.5 Hz, 2H), 3.03–3.00 (m, 2H), 1.35 (t, J = 6.8 Hz, 3H), 1.28 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 169.5, 167.6, 151.7, 148.7, 136.7, 136.1, 132.6, 127.1, 123.9, 122.7, 118.0, 112.2, 111.9, 102.0, 86.3, 77.2, 60.4, 59.1, 23.8, 14.5, 14.3. HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{25}N_2O_4$ 369.1814; found 369.1842.

General Procedure for the Synthesis of *N*–Styryl Carbazole/Aza-carbazole/γ–carbolines with Aliphatic Alkynes (6a–f): In an oven dried pressure tube, to a solution of carbazole/aza-carbazole/γ–carbolines **1** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (1.0 equiv, 28mg, 0.5 mmol) and alkynes **2aa–fa** (0.5 mmol) were added. The resulting reaction mixture was heated at 120 °C for 2 h. Progression of the reaction was monitored by TLC, while noticing complete consumption of alkynes, reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel mesh size 100–200 (hexane).

9-Vinyl-9H-carbazole (***6a***). The product was obtained as a brown needles (59.8 mg, 62% yield), mp: 101–103 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.49–7.45 (m, 2H), 7.42–7.39 (m, 1H), 7.34–7.30 (m, 1H), 7.29–7.27 (m, 2H), 5.55 (d, J = 16.7 Hz, 1H), 5.16 (d, J = 9.9 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.3, 129.5, 126.2, 120.6, 120.2, 114.1, 110.4, 102.1; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{14}H_{12}N$ 194.0970; found 194.0971.

(Z)-9-(3-Phenoxyprop-1-en-1-yl)-9H-carbazole (***6b***). The product was obtained as a yellow semi–solid (97.1 mg, 65% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.42–7.35 (m, 4H), 7.19–7.15 (m, 4H), 6.94 (t, J = 6.8 Hz, 1H), 6.78 (d, J = 9.1 Hz, 2H), 6.51–6.48 (m, 1H), 5.48–5.41 (m, 1H), 4.86–4.84 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 156.7, 145.1, 140.1, 129.6, 125.7, 123.14, 123.05, 120.4, 119.1, 116.8, 108.7, 106.7, 40.7; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{18}NO$ 300.1388; found 300.1382.

(Z)-3-Bromo-9-(2-(cyclohex-1-en-1-yl)vinyl)-9H-carbazole (***6c***). The product was obtained as a light yellow semi–solid (112.3 mg, 64% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.13 (m, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.43–7.41 (m, 1H), 7.37–7.34 (m, 1H), 7.19–7.14 (m, 3H), 7.03 (d, J = 9.1 Hz, 1H), 6.56 (d, J = 9.9 Hz, 1H), 6.04–6.00 (m, 1H), 2.10–2.07 (m, 2H), 1.86–1.83 (m, 2H), 1.51–1.46 (m, 4H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 140.1, 138.4, 134.8, 132.9, 128.4, 126.4, 124.7, 124.3, 123.9, 123.1, 122.0, 120.5, 119.6, 112.0, 111.2, 110.0, 26.4, 25.4, 22.7, 22.3; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{19}BrN$ 352.0701; found 352.0701.

(Z)-3,6-Dibromo-9-(2-cyclopropylvinyl)-9H-carbazole (***6d***). The product was obtained as a light brown semi–solid (116.4 mg, 60% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06–8.04 (m, 2H), 7.50–7.47 (m, 1H), 7.45–7.43 (m, 1H), 7.28–7.24 (m, 2H), 7.01–6.98 (m, 1H), 6.53–6.50 (m, 1H), 0.82–0.80 (m, 1H), 0.78–0.73 (m, 2H), 0.52–0.50 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.3, 136.3, 129.2, 123.04, 123.00, 114.1, 112.1, 112.0, 14.1, 8.0, 7.5; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{17}H_{14}Br_2N$ 389.9493; found 389.9493.

(Z)-9-(4-Phenylbut-1-en-1-yl)-9H-pyrido[2,3-b]indole (***6e***). The product was obtained as a pale yellow needles (107.2 mg, 72% yield), mp: 90–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45–8.43 (m, 1H), 8.24 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.45–7.44 (m, 2H), 7.21–7.17 (m, 4H), 7.12–7.09 (m, 3H), 6.36 (d, J = 16.0 Hz, 1H), 6.21–6.14 (m, 1H), 4.54 (t, J = 7.6 Hz, 2H), 2.74 (q, J = 6.8 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 145.9, 139.5, 137.3, 132.1, 128.6, 128.4, 128.1, 128.0, 127.1, 126.71, 126.66, 126.0, 121.1, 120.4, 119.7, 115.0, 109.3, 41.4, 32.7; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{19}N_2$ 299.1548; found 299.1544.

(Z)-5-(3-Methoxyprop-1-en-1-yl)-2-methyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***6f***). The product was obtained as a orange semi–solid (83.2 mg, 65% yield), ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.41–7.38 (m, 2H), 7.29 (d, J = 9.1 Hz, 1H), 7.13 (d, J = 9.9 Hz, 1H), 7.08–7.04 (m, 1H), 6.48 (d, J = 12.9 Hz, 1H), 4.57–4.56 (m, 2H), 3.68–3.69 (m, 2H), 3.44 (s, 3H), 2.88–2.84 (m, 4H), 2.56 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 149.6, 148.1, 136.1, 132.9, 125.6, 120.6, 118.8, 117.6, 109.0, 98.5, 55.8, 52.4, 51.7, 45.6, 41.3, 22.9; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{21}N_2O$ 257.1654; found 257.1648.

General Procedure for the Synthesis of Deuteurated (*E*) and (Z) *N*–Styryl Carbazole/Aza-carbazole/γ–carbolines (7a–d): In an oven dried pressure tube, to a solution of carbazole/aza-carbazole/γ–carbolines **1** (0.5 mmol) in 2.0 mL of DMSO–d_6, finely crushed KOH (0.5 equiv, 14mg, 0.25 mmol) and alkynes **2a** and **2r** (0.5 mmol) were added. The resulting reaction mixture was heated at 120 °C for 0.25 h–0.5 h. Progression of the reaction was monitored by TLC, while noticing complete consumption of alkynes, reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel mesh size 100–200 (hexane).

(Z)-9-Styryl-9H-carbazole (***7a***). The product was obtained as a brown needles (97.5 mg, 72% yield), mp: 91–93 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 2H), 7.34–7.31 (m, 2H), 7.28–7.21 (m, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.11–7.05 (m, 5H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 139.2, 134.7, 128.7, 128.3, 127.8, 126.3, 125.9, 124.0, 120.7, 120.2, 120.1, 111.1; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{14}D_2N$ 272.1408; found 272.1406.

(Z)-9-Styryl-9H-pyrido[2,3-b]indole (***7b***). The product was obtained as a light yellow crystalline needles (102.0 mg, 75% yield), mp: 120–122 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51–8.49 (m, 1H), 8.35–8.33 (m, 1H), 8.06–8.04 (m, 1H), 7.28–7.27 (m, 1H), 7.24–7.22 (m, 2H), 7.10–7.04

(m, 5H), 6.99 (d, *J* = 8.3 Hz, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 151.6, 146.5, 137.5, 134.8, 128.7, 128.20, 128.16, 127.8, 126.7, 126.6, 121.5, 120.8, 120.7, 116.9, 116.3, 112.2; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{19}H_{13}D_2N_2$ 273.1361; found 273.1353.

(Z)-2-Methyl-5-styryl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indole (***7c***).The product was obtained as a light brown needles (105.1 mg, 72% yield), mp: 142–144 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.33 (m, 1H), 7.06–7.04 (m, 2H), 7.02–7.00 (m, 2H), 6.92–6.89 (m, 2H), 3.62 (s, 2H), 2.63–2.60 (m, 2H), 2.51–2.48 (m, 2H), 2.43 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 135.5, 134.6, 133.1, 128.8, 128.5, 128.4, 127.8, 126.7, 126.4, 125.7, 125.6, 121.3, 119.9, 117.4, 110.8, 110.3, 52.4, 51.6, 45.6, 23.3; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{17}D_4N_2$ 293.1956; found 293.1959.

(E)-9-(4-(Trifluoromethyl)styryl)-9H-carbazole (***7d***). The product was obtained as a off-white needles (110.0 mg, 65% yield), mp: 90–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.64–7.55 (m, 3H), 7.51–7.47 (m, 1H), 7.34–7.32 (m, 2H), 7.16–7.10 (m, 1H), 7.04–7.01 (m, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 139.3, 128.8, 126.4, 126.1, 125.8, 125.7 , 125.3 (q, *J* = 3.8 Hz, 1C), 124.4, 121.2, 120.4, 116.6, 110.6; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{13}D_2F_3N$ 340.1282; found 340.1276.

General procedure for the synthesis of mono and bis–hydroaminated–heterocycles (8a–d): In an oven dried pressure tube, to a solution of *N*–heterocycles **1a** and **1h** (0.5 mmol) in 2.0 mL of DMSO, finely crushed KOH (0.5 equiv, 14mg, 0.25 mmol) and alkynes **2w**–**y** (0.25 mmol) were added under inert atmosphere for mono hydroamination, however; for bis-styrylated product 1.2 equiv of KOH was used. The resulting reaction mixture was heated at 120 °C for 0.5–36 h. Progression of the reaction was monitored by TLC, while noticing complete

consumption of alkynes, reaction was brought to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel mesh size 100–200 (hexane).

(Z)-9-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)-9H-carbazol-2-ol (***8a***). The product was obtained as a pale yellow needles (96.9 mg, 70% yield), mp: 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (br s, 1H), 7.93–7.88 (m, 3H), 7.32–7.28 (m, 2H), 7.18–7.14 (m, 1H), 6.95 (s, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.57–6.55 (m, 1H), 4.96–4.93 (m, 1H), 4.31–4.25 (m, 2H), 4.18–4.14 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 156.2, 144.3, 140.3, 139.7, 125.2, 123.1, 121.1, 119.8, 119.7, 119.2, 110.5, 109.6, 107.3, 98.4, 79.8, 74.3, 62.8, 57.2; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{18}H_{16}NO_2$ 278.1181; found 278.1181.

(E)-9-(3-Ethynylstyryl)-9H-pyrido[2,3-b]indole (***8b***). The product was obtained as a yellow semi–solid (91.1 mg, 62% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 6.1 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 8.03–7.99 (m, 2H), 7.77 (d, J = 8.3 Hz, 1H), 7.65 (s, 1H), 7.55 (d, J = 14.5 Hz, 1H), 7.51–7.47 (m, 2H), 7.32–7.27 (m, 3H), 7.22–7.20 (m, 1H), 3.04 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 146.3, 138.3, 137.1, 130.4, 129.4, 128.7, 128.1, 127.4, 126.4, 125.7, 122.8, 122.5, 121.6, 121.5, 121.1, 118.4, 117.2, 116.9, 111.0, 83.6, 77.2; HRMS (ESI$^-$TOF) *m/z*: $(M+H)^+$ Calcd for $C_{21}H_{15}N_2$ 295.1235; found 295.1229.

(E)-9-(4-Ethynylstyryl)-9H-carbazole (***8c***). The product was obtained as a pale yellow semi–solid (95.2 mg, 65% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 2H), 7.70–7.64 (m, 4H), 7.44 (t, J = 8.3 Hz, 3H), 7.41–7.38 (m, 2H), 7.25 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 14.5 Hz, 1H), 3.08 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.4, 132.6, 132.0, 128.6, 126.4,

125.5, 124.3, 124.2, 121.0, 120.4, 118.1, 110.6, 83.7, 77.8; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{22}H_{16}N$ 294.1283; found 294.1252.

1-((E)-2-(9H-Carbazol-9-yl)vinyl)-4-((Z)-2-(9H-carbazol-9-yl)vinyl)benzene (***8d***). The product was obtained as a light yellow semi–solid (138.0 mg, 60% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.09 (m, 2H), 8.06–8.02 (m, 2H), 7.77–7.74 (m, 1H), 7.65–7.62 (m, 2H), 7.56 (d, J = 13.7 Hz, 1H), 7.53–7.49 (m, 1H), 7.46–7.42 (m, 1H), 7.41–7.37 (m, 1H), 7.34–7.28 (m, 4H), 7.25–7.22 (m, 5H), 7.11–7.06 (m, 2H), 6.92 (d, J = 9.9 Hz, 1H), 6.83–6.80 (m, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.4, 139.2, 139.1, 139.0, 129.3, 128.7, 126.3, 126.0, 125.9, 125.6, 125.2, 124.1, 120.8, 120.3, 120.2, 120.1, 118.7, 111.2, 111.1, 110.6; HRMS (EI–TOF) *m/z*: $(M)^+$ Calcd for $C_{34}H_{24}N_2$ 460.1939; found 460.1938.

3,6-Bis((E)-4-chlorostyryl)-9-((Z)-4-methylstyryl)-9H-carbazole (***9a***). The product was obtained as a light yellow needles (166.5 mg, 60% yield), mp: 150–152 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 7.47–7.45 (m, 4H), 7.35–7.32 (m, 4H), 7.27–7.23 (m, 4H), 7.17 (d, J = 8.3 Hz, 2H), 7.11–7.07 (m, 2H), 6.96–6.90 (m, 4H), 6.84 (d, J = 9.1 Hz, 1H), 6.67 (d, J = 9.1 Hz, 1H), 2.22 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.5, 139.3, 136.3, 132.7, 131.6, 129.9, 129.7, 129.1, 128.8, 128.7, 127.4, 125.4, 125.0, 124.2, 120.6, 118.4, 114.0, 111.5, 22.7; HRMS (ESI–TOF) *m/z*: $(M+H)^+$ Calcd for $C_{37}H_{28}Cl_2N$ 556.1599; found 556.1595.

(Z)-9-(4-Methylstyryl)-3,6-diphenyl-9H-carbazole (***9b***). The product was obtained as a off–white needles (147.9 mg, 68% yield), mp: 141–143 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.36 (m, 2H), 7.76–7.71 (m, 4H), 7.64–7.59 (m, 2H), 7.49–7.43 (m, 4H), 7.36–7.33 (m, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.03–7.01 (m, 2H), 6.94–6.92 (m, 2H), 6.88 (d, J = 8.3 Hz, 1H), 6.67 (d, J = 8.3 Hz, 1H), 2.23 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 141.8, 139.3, 137.9, 133.8, 131.8, 129.1,

128.8, 127.3, 126.8, 126.6, 125.6, 124.6, 121.0, 118.7, 111.5, 21.3; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{33}H_{26}N$ 436.2065; found 436.2045.

(Z)-3,6-Bis((4-methoxyphenyl)ethynyl)-9-(4-methylstyryl)-9H-carbazole (**9c**)**.** The product was obtained as a brown semi–solid (168.3 mg, 62% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.164–8.160 (m, 2H), 7.48 (d, J = 9.1 Hz, 1H), 7.44–7.43 (m, 2H), 7.42–7.41 (m, 2H), 7.27–7.22 (m, 3H), 7.07 (d, J = 8.3 Hz, 2H), 6.94 (s, 1H), 6.80–6.79 (m, 2H), 6.76–6.75 (m, 1H), 6.73–6.70 (m, 2H), 6.63 (d, J = 9.1 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 3.75 (s, 6H), 2.14 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.4, 139.0, 138.2, 136.6, 132.9, 130.5, 129.8, 129.1, 128.6, 127.7, 123.6, 115.4, 114.0, 113.8, 113.5, 111.2, 88.9, 88.0, 55.3, 55.1, 21.2; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{39}H_{30}NO_2$ 544.2277; found 544.2267.

(Z)-3-Bromo-6-((4-methoxyphenyl)ethynyl)-9-(4-methylstyryl)-9H-carbazole (***9d***). The product was obtained as a yellow needles (164.4 mg, 67% yield), mp: 90–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 9.1 Hz, 2H), 7.44–7.39 (m, 4H), 7.04 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 9.1 Hz, 1H), 6.81–6.77 (m, 6H), 6.68 (d, J = 8.3 Hz, 1H), 6.57 (d, J = 9.1 Hz, 1H), 3.73 (s, 3H), 2.12 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 159.4, 138.9, 138.23, 138.17, 132.9, 131.2, 130.0, 129.2, 129.0, 128.6, 127.9, 125.0, 123.6, 123.0, 122.7, 120.1, 115.7, 115.4, 114.0, 113.4, 112.6, 111.2, 88.7, 88.1, 55.3, 21.2; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{30}H_{23}BrNO$ 492.0963; found 492.0935.

(Z)-3-((4-Ethylphenyl)ethynyl)-6-((4-methoxyphenyl)ethynyl)-9-(4-methylstyryl)-9H-carbazole (***9e***). The product was obtained as a yellow needles (148.7 mg, 55% yield), mp: 84–86 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.24 (m, 2H), 7.51–7.47 (m, 5H), 7.19 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 9.1 Hz, 2H), 6.90–6.86 (m, 7H), 6.83 (d, J = 9.1 Hz, 1H), 6.69 (d, J = 9.1 Hz, 1H), 3.83 (s,

3H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 159.4, 144.3, 139.1, 139.0, 138.2, 132.9, 131.5, 131.3, 129.9, 129.8, 129.2, 128.6, 127.9, 127.72, 127.69, 123.8, 123.7, 123.4, 120.2, 115.8, 115.5, 115.3, 114.0, 113.8, 113.5, 111.2, 89.6, 88.9, 88.3, 88.0, 55.3, 28.8, 21.2, 15.4; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{40}H_{32}NO$ 542.2484; found 542.2490.

9-Phenethyl-9H-carbazole (***9f***). The product was obtained as a yellow needles (81.3 mg, 60% yield), mp: 100–102 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.45–7.41 (m, 2H), 7.34–7.32 (m, 2H), 7.29–7.17 (m, 7H), 4.51 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 140.1, 138.7, 128.8, 128.6, 126.6, 125.6, 122.8, 120.3, 118.9, 108.5, 44.9, 35.2; HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{20}H_{18}N$ 272.1439; found 272.1443.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR and HRMS spectra for compounds are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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