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A General Method for the Synthesis of 5*H*-Benzo[*b*]-, Carbazolo[2,3-*b*]- and Indolo[2,3-*b*]carbazole Derivatives *via* Copper(II) Triflate-Catalyzed Heteroannulation

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Abstract: A straightforward approach for the construction of 5*H*-benzo[*b*]-, carbazolo[2,3-*b*]- and indolo[2,3-*b*]carbazole derivatives has been developed by using copper(II) triflate-catalyzed heteroannulation.

Keywords: carbazole derivatives; copper(II) triflate; heteroannulation; heterocycles

Introduction

Over the past few years, carbazole and its fused aromatic systems were found to display a wide range of attractive biological activities.[1] Of its fused aromatic systems, syntheses of benzannulated and heteroannulated carbazole analogues are vital as such compounds are not found in abundance in natural sources. They exhibit promising biological activities,[2] especially antitumor activity.[3] In particular, benzo[*a*]carbazole derivatives have been found to have binding affinities for the estrogen receptor, and inhibit the mammary tumors of rats.[4a] Benzo[*b*]carbazole derivatives **1** and **2** (Figure 1) show cytostatic activity against leukemia type L 1210 cell culture[4b] and have a potential bifunctional nucleic acid intercalating property,[4c] respectively.

Ever since the first isolation of indolocarbazole in 1977, organic chemists have been interested in the synthesis of indolocarbazole and its derivatives due to their biological activities.[5] 6-Formylindolo[3,2-*b*]carbazole **3** and 6,12-diformylindolo[3,2-*b*]carbazole **4** (Figure 1) are reported to be highly efficient ligands for the Ah receptor.[6] Carbazolocarbazole derivatives are being explored in the field of organic electronics,[7] anion binding studies[8] and organic dyes.[9] Although the structure of carbazolocarbazole was first reported in 1965, these derivatives did not receive much attention and only a few reports were available concerning their synthesis.[7–9]

In recent years, there has been an immense interest in the cyclization of phenylacetylenes that have a halo[10] or a carbonyl or an imino group in an *ortho* position by employing various catalysts.[11,12,15] Similarly, Lewis acid-mediated domino reactions have been proven to be a powerful method in the synthesis of

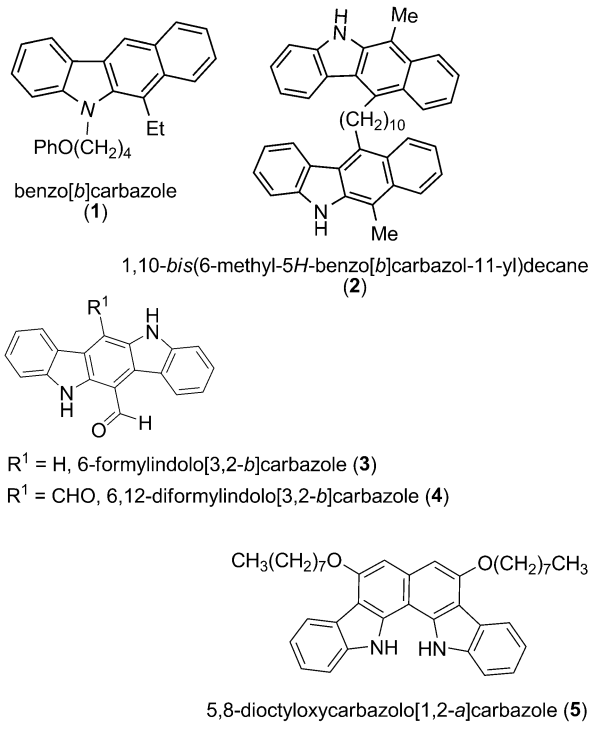


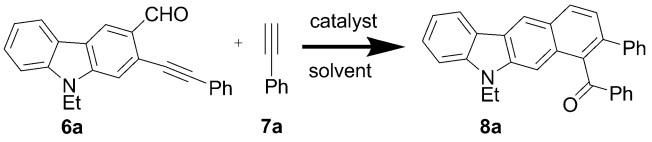
Figure 1. Structures of important benzo-, indolo-, and carbazolocarbazole derivatives.

a wide variety of polycyclic heterocycles.[14,19] Yamamoto's group described the iodine-mediated electrophilic cyclization of 2-alkynyl-1-methylene azide,[13] Lewis acid-catalyzed benzannulation of *o*-alkynyl-(oxo)benzenes with alkynes,[14a] alkenes[14b] and enols.[14c] Barluenga et al. developed a new metal-free protocol for consecutive C–O and C–C bond formation using $IPy_2 \cdot BF_4$.[15] Especially, Larock et al. reported the reaction of alkynes having a *tert*-butylimino group close to the carbon-carbon triple bond catalyzed by copper,[16a–c] palladium;[16d,e] and cyclization induced by electrophiles.[16f] Jana et al. developed an intramolecular alkyne-carbonyl metathesis under iron-catalyzed conditions.[17] Very recently, Cao and colleagues have reported a Pd-catalyzed sequential reaction for the synthesis of *δ*-carbolines using Larock heteroannulation/elimination/electrocyclization and oxidative aromatization.[18]

However, to the best of our knowledge, very few reports have been published in the literature for the annulation of indole and 2-ethynylbenzaldehyde,[20a,b] and the reaction of heteroarylalkynylaldehyde with indoles was unexplored. Thus, the development of synthetic methods for annulated carbazoles is sure to open up new opportunities to utilize these compounds as organic materials as well as in new biological applications.

Here, we communicate a simple and facile strategy for the synthesis of benzo[*b*]-, carbazolo[2,3-*b*]- and indolo[2,3-*b*]carbazole derivatives *via* copper(II) triflate-catalyzed heteroannulation.

Table 1. Optimization of the reaction conditions.[a]



6a **7a** **8a**

Entry	Catalyst	Solvent	Time [h]	Yield [%][b]
1[c]	$Cu(OTf)_2$	DCE	10	70
2	**$Cu(OTf)_2$**	**DCE**	**5**	**92**
3	$Cu(OTf)_2$	CH_3CN	5	68
4	$Cu(OTf)_2$	THF	5	70
5	$Cu(OTf)_2$	toluene	5	45
6	$CuBr_2$	DCE	5	64
7	$CuCl_2$	DCE	5	53
8	CuBr	DCE	5	62
9	CuI	DCE	5	68
10	AgOTf	DCE	5	51
11	$FeCl_3$	DCE	5	NR
12	$La(OTf)_3$	DCE	5	trace
13	-	DCE	5	NR
14	$Cu(OTf)_2$	DCE	5	NR[d]/trace[e]

[a] *Reaction conditions:* **6a** (0.5 mmol), **7a** (1.0 mmol), solvent (5 mL), catalyst (15 mol%), 80 °C. NR: no reaction.
[b] Isolated yields.
[c] 10 mol% catalyst was used.
[d] Reaction was carried out at room temperature.
[e] Reaction was carried out at 50 °C.

Result and Discussion

We began our investigation by optimizing the reaction between **6a** and **7a** using various catalysts and solvents. The results are summarized in Table 1.

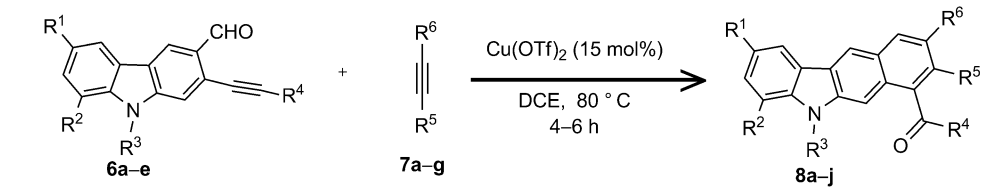
While using 10 mol% $Cu(OTf)_2$, we got the product **8a** with lower yield in longer reaction time (Table 1, entry 1). So, we increased the amount of catalyst to 15 mol%. Under these conditions, the reaction proceeded smoothly and benzocarbazole **8a** was obtained in 92% yield (Table 1, entry 2). We also screened other solvents, such as CH_3CN, THF, toluene, etc. (Table 1, entries 3, 4, and 5), however only inferior results were observed. Other catalysts gave the product in low yield (Table 1, entries 6–12). In the absence of a catalyst, no cyclization was observed (Table 1, entry 13).

As shown in Table 1, we conclude that best result was obtained with 15 mol% $Cu(OTf)_2$ as a catalyst and dichloroethane as solvent at 80 °C. Employing the optimized reaction conditions, we successfully synthesized various benzo[*b*]carbazole derivatives **8a–j**.

As shown in Scheme 1, substrates containing substituents like phenyl, *p*-tolyl, diphenyl, and alkyl on the acetylene (Scheme 1, **7a–e**) could be handled without any trouble and also gave the products in good yields. With arylalkynes bearing electron-withdrawing groups (Scheme 1, **7f** and **7g**), we were unable to separate the corresponding product due to the complex mixtures as found in TLC. The structure of the product **8a** was unambiguously confirmed by the single crystal X-ray diffraction analysis[21] and an ORTEP diagram of **8a** is shown in Figure 2.

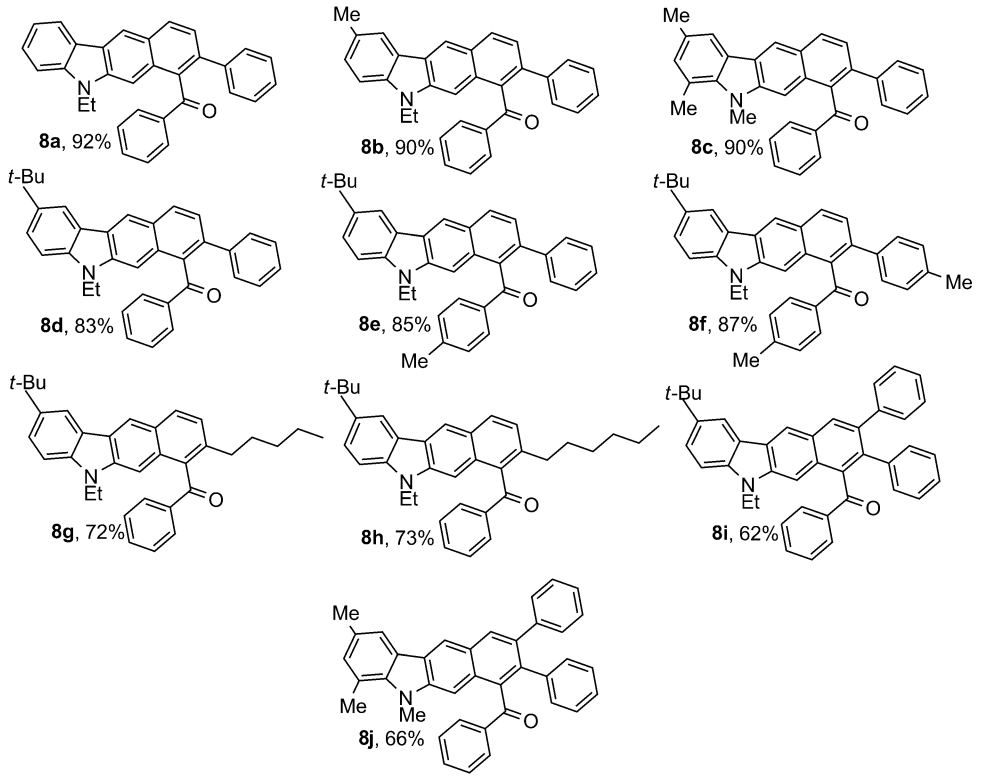
Based on the reported literature,[14] a possible mechanism for the formation of benzocarbazole derivatives (**8a–j**) has been proposed in Scheme 2. As outlined in Scheme 2, $Cu(OTf)_2$ coordinates with triple bond of **6** to enhance the electrophilicity of the alkyne. Subsequently, nucleophilic attack of the carbonyl oxygen followed by cycloaddition with alkyne delivers the benzo[*b*]carbazole derivatives **8**.

We expected that a similar kind of cyclization could be done with 2-alkynylcarbazole-3-carbaldehydes (**6a–f**) and indoles (**9a–g**) using the copper catalyst. As expected, we got the desired product **10a** in good yield (85%) by employing $Cu(OTf)_2$ (10 mol%) as a catalyst and dichloroethane as a solvent at 80 °C (Table 2, entry 3).



6a: R^1 = H, R^2 = H, R^3 = Et, R^4 = Ph
6b: R^1 = Me, R^2 = H, R^3 = Et, R^4 = Ph
6c: R^1 = Me, R^2 = Me, R^3 = Me, R^4 = Ph
6d: R^1 = *t*-Bu, R^2 = H, R^3 = Et, R^4 = Ph
6e: R^1 = *t*-Bu, R^2 = H, R^3 = Et, R^4 = *p*-tolyl

7a: R^5 = Ph, R^6 = H
7b: R^5 = *p*-tolyl, R^6 = H
7c: R^5 = -$(CH_2)_4CH_3$, R^6 = H
7d: R^5 = -$(CH_2)_5CH_3$, R^6 = H
7e: R^5, R^6 = Ph
7f: R^5, R^6 = COOMe
7g: R^5 = *p*-$NO_2C_6H_4$, R^6 = H



Scheme 1. $Cu(OTf)_2$-catalyzed cyclization of 2-(alkynyl)carbazole-3-carbaldehydes (**6a–e**) with different arylacetylenes (**7a–g**). Unless otherwise noted, all the reactions were carried out in dichloroethane (5.0 mL) as a solvent at 80 °C using **6a–e** (0.5 mmol) and **7a–g** (1.0 mmol) in the presence of $Cu(OTf)_2$ (15 mol%). Isolated yields after column chromatography are given.

This result prompted us to optimize the reaction conditions. When using $CuBr_2$ as a catalyst, the yield of the anticipated product was low with a trace amount of inseparable by-products (Table 2, entry 7). We could not improve the yield of the product while screening other copper catalysts. To extend this methodology further, we carried out the reaction of 2-alkynylcarbazole-3-carbaldehydes (**6a–f**) with various indoles (**9a–g**) in the presence of $Cu(OTf)_2$ (10 mol%) under the optimized conditions. The scope of this reaction is outlined in Scheme 3.

Motivated by these results, we turned our attention next to the synthesis of indolo[2,3-*b*]carbazole derivatives using 2-alkynylindole-3-carbaldehyde and indole. Here again, we started our synthesis by screening various copper catalysts. Among them, 10 mol% $Cu(OTf)_2$ gave the expected product **12a** in DCE as a solvent. After careful column chromatography, indolo[2,3-*b*]carbazole **12a** was isolated in moderate yield. It was possible to slightly increase the yield of the product as R^1 was an electron-withdrawing substituent (Scheme 4, **12b–d**).

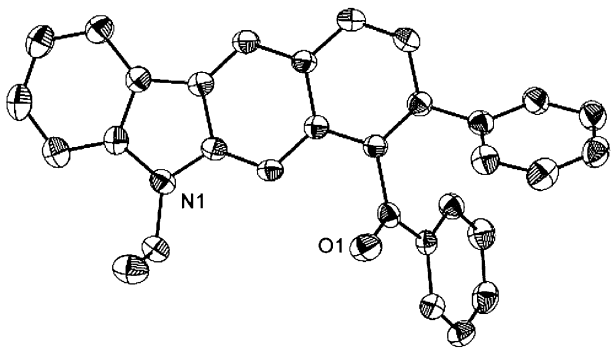


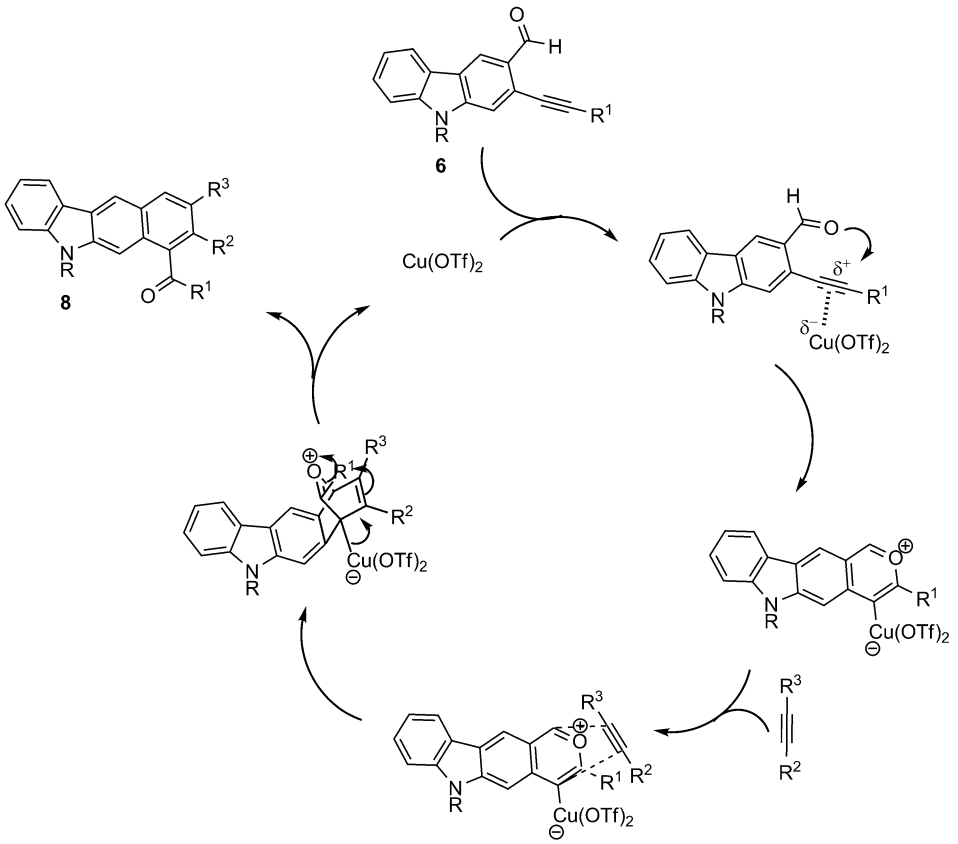
Figure 2. ORTEP diagram of **8a**. Hydrogen atoms are omitted for clarity.

In ^{1}H NMR spectra of **12a–d**, a singlet around $\delta =$ 8.50–9.30 ppm which corresponds to the C-12 proton of the indolo[2,3-*b*]carbazole derivatives clearly indicate the formation of products (see the Supporting Information). Reaction of **11a** with indole did not afford the desired product. The possible mechanism for the coupling of indole and 2-alkynylcarbazole-3-carbaldehydes (**6a–f**), 2-alkynylindole-3-carbaldehydes (**11a–c**) is depicted in Scheme 5 based on the literature.[14,20]

In order to understand the reaction pathway, we trapped the intermediate **13** (Scheme 6) by performing a reaction between 2-alkynylcarbazole-3-carbaldehyde (**6b**) and indole (**9a**). Employing 10 mol% $Cu(OTf)_2$ in DCE as a solvent at room temperature gave the intermediate **13** in trace amount. While heating, we were unable to trap the intermediate **13** because **10d** was formed at faster rate. So, we changed the reaction conditions (10 mol% $PdCl_2$, DMSO as a solvent at room temperature) to trap the intermediate **13**. As shown in Scheme 6, the intermediate **13** was prepared in 78% yield and subjected to reaction under the standard conditions [10 mol% $Cu(OTf)_2$ and 1,2-dichloroethane as a solvent], and this also gave carbazolocarbazole **10d** in good yield (85%). These results clearly led to the conclusion that the domino process proceeds through the trapped intermediate **13.**

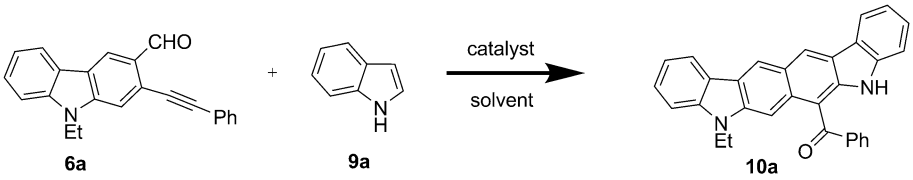
Conclusions

In summary, we have demonstrated a simple and efficient methodology for the synthesis of benzo[*b*]-, carbazolo[2,3-*b*]-, and indolo[2,3-*b*]carbazole derivatives in moderate to good yields. The scope of this



Scheme 2. Possible mechanism for the formation of benzocarbazole derivatives.

Table 2. Optimization of copper-catalyzed cyclization of **6a** with indole.[a]



Entry	Catalyst	Solvent	Temp. [°C]	Time [h]	Yield [%][b]
1	$Cu(OTf)_2$	DCE	r.t.	12	0
2	$Cu(OTf)_2$	DCE	50	10	68
3	**$Cu(OTf)_2$**	**DCE**	**80**	**1**	**85**
4	$Cu(OTf)_2$	CH_3CN	80	3	60
5	$Cu(OTf)_2$	THF	80	3	62
6	$Cu(OTf)_2$	toluene	80	5	52
7	$CuBr_2$	DCE	80	3	71
8	CuBr	DCE	80	3	68
9	CuI	DCE	80	3	63
10	CuCl	DCE	80	3	48
11	$CuCl_2$	DCE	80	3	54
12	–	DCE	80	3	trace

[a] *Reaction conditions:* **6a** (0.5 mmol), **9a** (0.5 mmol), solvent (5 mL), catalyst (10 mol%).
[b] Isolated yields.

synthetic route is general. This process can be applicable to wide range of functional groups, affording the corresponding benzo[*b*]-, carbazolo[2,3-*b*]-, and indolo[2,3-*b*]carbazole derivatives. With high conjugation and functional groups like carbonyl near to the free NH moiety, these molecules might be useful in the field of biology and organic materials.

Experimental Section

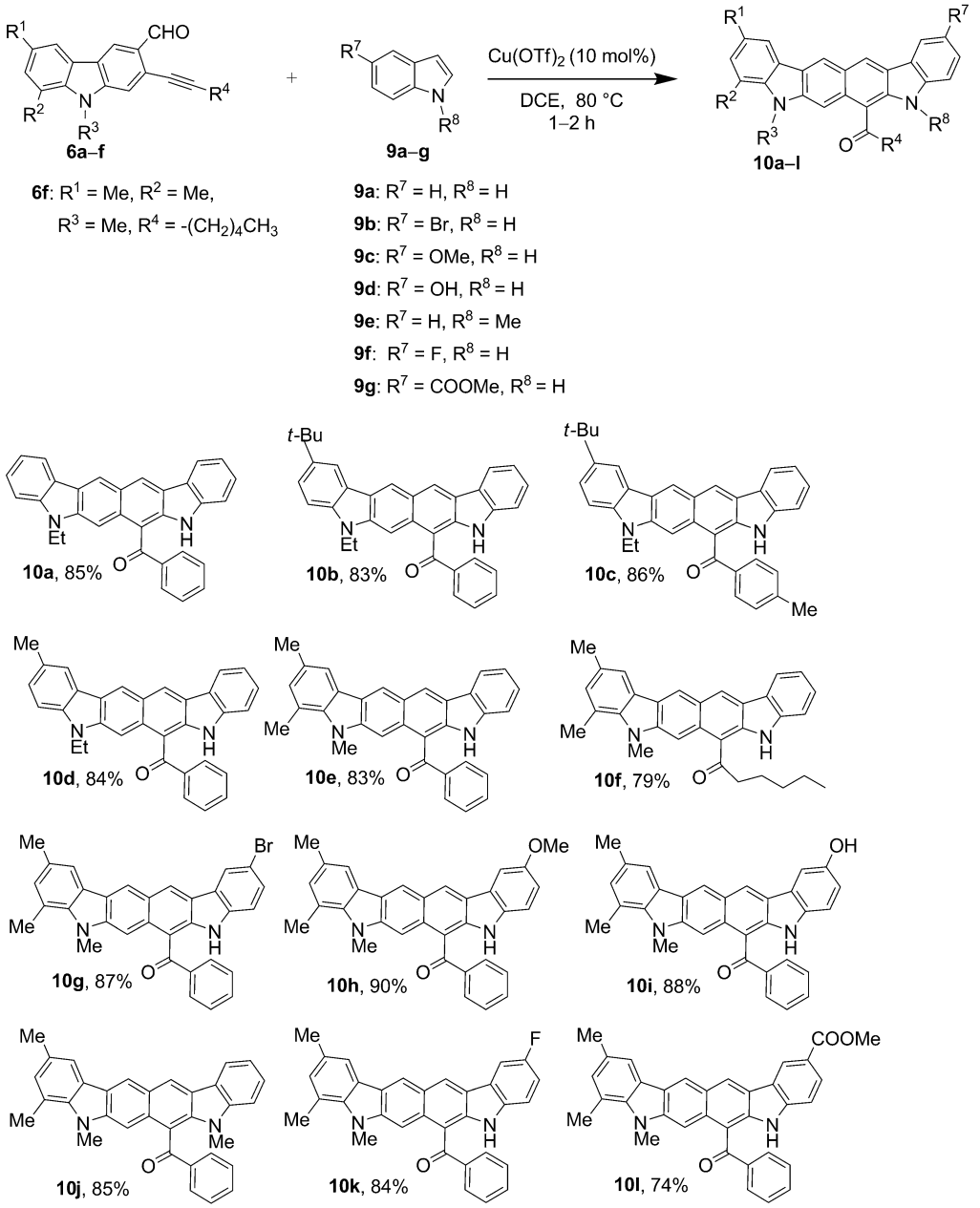
General Information

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, or at 500 and 125 MHz, respectively. Chemical shifts are calculated in ppm downfield from TMS ($\delta = 0$) for ^{1}H NMR, and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) and DMSO-d_6 ($\delta = 39.51$) for ^{13}C NMR. Data are presented as follows: chemical shift, multiplicity (bs = broad singlet, s = singlet, d = doublet, dd = doublet doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration. IR spectra were recorded on a JASCO FT/IR-5300 instrument. Elemental analysis was carried out in a Thermo Finnigan Flash EA 1112 analyzer in the School of Chemistry, University of Hyderabad. X-ray diffraction measurements were carried out at 298 K on an automated diffractometer using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on an instrument equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($l = 0.71073$ Å). Melting points were measured in open capillary tubes and are uncorrected. All the obtained products were purified by column chromatography using silica gel (100–200 mesh). All reaction solvents used were of GR grade and used without drying unless mentioned. All other commercial reagents were used as received.

2-Alkynylcarbazole-3-carbaldehydes (**6a–f**) were prepared from 2-bromocarbazoles as methods developed from our laboratory[22a,b] and 2-alkynylindole-3-carbaldehydes (**11a–c**) were prepared according to reported literature methods.[16c,22c]

General Procedure for the Synthesis of Benzo[*b*]carbazole Derivatives

An oven-dried 10-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with 0.5 mmol of 9-ethyl-2-(2-phenylethynyl)-9*H*-carbazole-3-carbaldehyde (**6a**), 15 mol% of $Cu(OTf)_2$, 1.0 mmol of phenylacetylene (**7a**) and 5 mL of dry 1,2-dichloroethane. The reaction mixture was stirred at 80 °C. After 5 h, solvent and excess of phenylacetylene were removed under reduced pressure. The crude reaction mixture was then poured over water and extracted with EtOAc (3×20 mL). The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed. The residue was purified by column chromatography (10% ethyl acetate in hexanes) on silica gel to afford the product **8a**; yield: 92%. We followed the same proce-

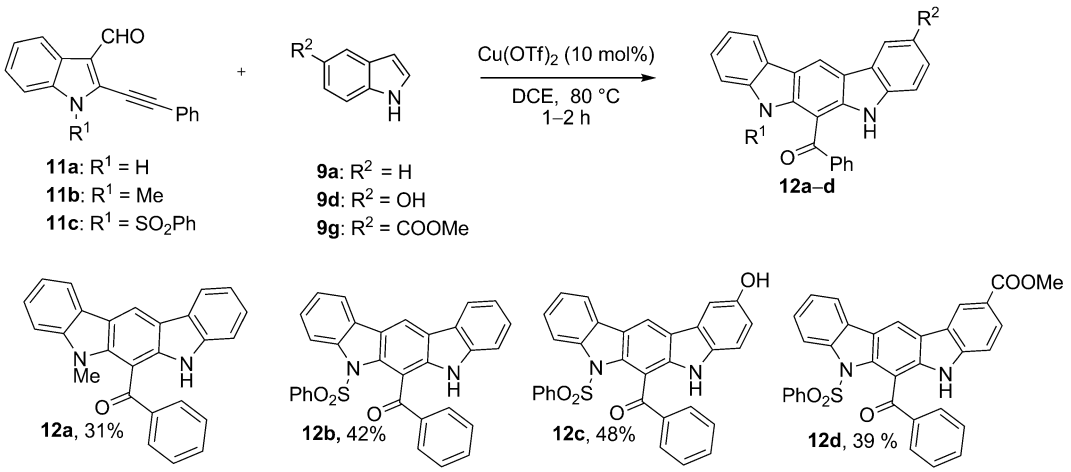


Scheme 3. $Cu(OTf)_2$-catalyzed cyclization of 2-(alkynyl)carbazole-3-carbaldehydes (**6a–f**) with indoles (**9a–g**). Unless otherwise noted, all the reactions were carried out in dichloroethane (5.0 mL) as a solvent at 80 °C using **6a–f** (0.5 mmol) and **9a–f** (0.5 mmol) in the presence of $Cu(OTf)_2$ (10 mol%). Isolated yields after column chromatography are given.

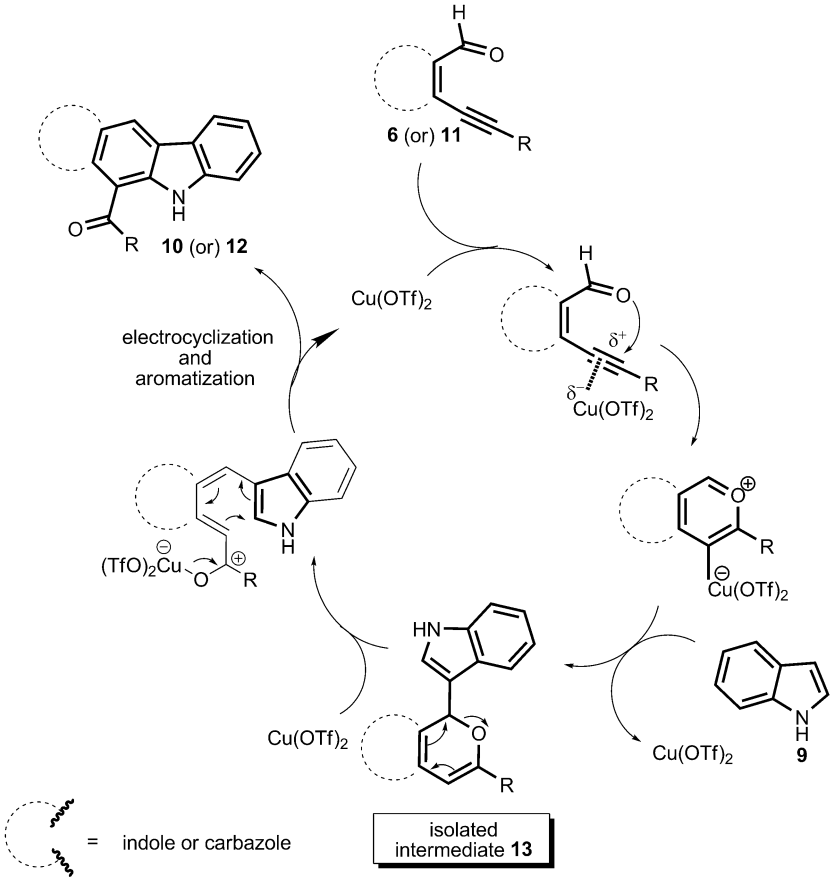
dure for the synthesis of other benzo[*b*]carbazole derivatives (**8b–8j**).

(5-Ethyl-8-phenyl-5*H*-benzo[*b*]carbazol-7-yl)(phenyl)-methanone (8a): Yield: 92%; mp 168–170 °C; IR (KBr): ν = 2910, 1720, 1590, 1060, 790 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.68 (s, 1H), 8.24 (t, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.42–7.36 (m, 4H), 7.30–7.22 (m, 5H), 7.18–7.16 (m, 1H), 4.27 (q, *J* = 6.8 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 200.8, 142.8, 140.9, 140.7, 138.5, 137.1, 134.3, 133.0, 130.3, 129.7, 129.6, 128.2, 128.1, 127.5, 127.2, 127.0, 125.6, 124.3, 122.5, 121.2, 119.2, 119.0, 108.3, 101.0 (aromatic C); 37.5, 13.1 (aliphatic C); LC-MS (positive mode): *m*/*z* = 426 ($M+H^+$); anal. calcd. for $C_{31}H_{23}NO$: C 87.50, H 5.45, N 3.29%; found: C 87.41, H 5.51, N 3.22%.

(5-Ethyl-2-methyl-8-phenyl-5*H*-benzo[*b*]carbazol-7-yl)-(phenyl)methanone (8b): Yield: 90%; mp 156–158 °C; IR (KBr): ν = 2909, 1729, 1560, 1060, 881, 850 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.64 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.08 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.41–7.37 (m, 4H), 7.28–7.23

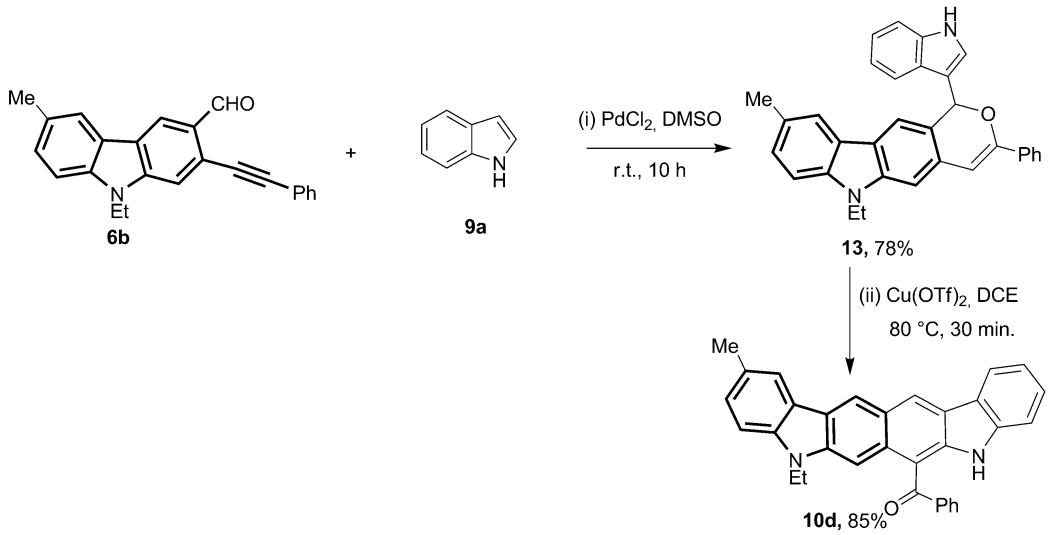


Scheme 4. $Cu(OTf)_2$-catalyzed cyclization of 2-alkynylindole-3-aldehydes (**11a–c**) with indoles (**9a**, **9d** and **9g**). Unless otherwise noted, all the reactions were carried out in dichloroethane (5.0 mL) as a solvent at 80 °C using **11a–c** (0.5 mmol) and **9a**, **9d** and **9g** (0.5 mmol) in the presence of $Cu(OTf)_2$ (10 mol%). Isolated yields after column chromatography are given.



Scheme 5. Possible mechanism for the formation of indolo and carbazolocarbazole derivatives.

(m, 5H), 7.19 (t, J=7.0 Hz, 1H), 4.26 (q, J=7.0 Hz, 2H), 2.59 (s, 3H), 1.32 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ=200.6, 141.0, 140.9, 138.6, 137.0, 134.3, 132.9, 130.2, 129.7, 129.6, 129.5, 128.7, 128.5, 128.4, 128.2, 128.1, 127.2, 126.9, 125.5, 124.1, 122.6, 121.3, 118.9, 108.0, 100.9 (aromatic C); 37.5, 21.3, 13.1 (aliphatic C); LC-MS (positive mode): m/z=440 ($M+H^+$); anal. calcd. for $C_{32}H_{25}NO$: C 87.44, H 5.73, N 3.19%; found: C 87.61, H 5.68, N 3.25%.



Scheme 6. Formation of intermediate **13** and its cyclization. *Reaction conditions*: (i) **6b** (0.5 mmol), **9a** (0.5 mmol), 10 mol% of $PdCl_2$, 5 mL DMSO; (ii) **13** (0.3 mmol), 10 mol% of $Cu(OTf)_2$, 4 mL DCE.

Phenyl(2,4,5-trimethyl-8-phenyl-5*H*-benzo[*b*]carbazol-7-yl)(phenyl)methanone (8c): Yield: 90%; mp 152–154 °C; IR (KBr): ν = 2928, 1722, 1490, 1070, 900 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.58 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.39–7.37 (m, 3H), 7.27–7.21 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.10 (s, 1H), 3.98 (s, 3H), 2.80 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 200.8, 142.9, 140.9, 140.5, 138.4, 136.8, 134.4, 133.0, 132.2, 130.1, 129.7, 129.6, 128.7, 128.2, 128.1, 127.2, 127.0, 125.5, 124.1, 123.2, 119.9, 119.0, 118.5, 101.1 (aromatic C); 32.6, 21.0, 20.1 (aliphatic C); LC-MS (positive mode): *m/z* = 440 ($M+H^+$); anal. calcd. for $C_{32}H_{25}NO$: C 87.44, H 5.73, N 3.19%; found: C 87.32, H 5.68, N 3.25%.

(2-*tert*-Butyl-5-ethyl-8-phenyl-5*H*-benzo[*b*]carbazol-7-yl)(phenyl)methanone (8d): Yield: 83%; mp 124–126 °C; IR (KBr): ν = 2920, 1722, 1585, 1290, 1060, 850 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.69 (s, 1H), 8.28 (d, *J* = 1.8 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.65 (m, 2H), 7.63 (dd, *J* = 8.8 & 2.0 Hz, 1H), 7.57 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.40–7.36 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25–7.21 (m, 4H), 7.18 (d, *J* = 7.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 200.7, 142.2, 141.1, 140.9, 138.6, 137.0, 134.3, 132.9, 130.2, 129.7, 129.6, 128.3, 128.2, 128.1, 127.2, 127.0, 125.9, 125.3, 124.1, 122.2, 118.9, 117.5, 107.8, 107.5, 100.9 (aromatic C), 37.5, 34.7, 32.0, 13.2 (aliphatic C); LC-MS (positive mode): *m/z* = 482 ($M+H^+$); anal. calcd. for $C_{35}H_{31}NO$: C 87.28, H 6.49, N 2.91%; found: C 87.14, H 6.38, N 3.05%.

(2-*tert*-Butyl-5-ethyl-8-phenyl-5*H*-benzo[*b*]carbazol-7-yl)(*p*-tolyl)methanone (8e): Yield: 85%; mp 120–122 °C; IR (KBr): ν = 2910, 1720, 1590, 1060, 850 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.70 (s, 1H), 8.31 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.64 (dd, *J* = 8.0 & 2.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.57 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.45 (s, 1H), 7.43 (s, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.29–7.26 (m, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.26 (q, *J* = 7.0 Hz, 2H), 2.31 (s, 3H), 1.52 (s, 9H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 200.3, 143.8, 142.1, 141.1, 141.0, 140.9, 136.7, 136.0, 134.5, 130.0, 129.8, 129.6, 129.0, 128.9, 128.1, 127.1, 127.0, 125.8, 125.2, 124.2, 122.2, 118.9, 117.5, 107.8, 101.0 (aromatic C), 37.5, 34.7, 32.0, 21.6, 13.2 (aliphatic C); LC-MS (positive mode): *m/z* = 496 ($M+H^+$); anal. calcd. for $C_{36}H_{33}NO$: C 87.24, H 6.71, N 2.83%; found: C 87.09, H 6.78, N 2.76%.

(2-*tert*-Butyl-5-ethyl-8-*p*-tolyl-5*H*-benzo[*b*]carbazol-7-yl)(*p*-tolyl)methanone (8f): Yield: 87%; mp 116–118 °C; IR (KBr): ν = 2910, 1720, 1470, 1580, 1080, 950 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.67 (s, 1H), 8.28 (d, *J* = 1.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.61 (m, 3H), 7.51 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.32 (m, 2H), 7.06 (m, 5H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H), 1.50 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 200.5, 143.9, 142.1, 141.0, 140.9, 138.1, 137.5, 136.8, 136.6, 136.0, 134.3, 129.9, 129.4, 129.0, 128.9, 126.8, 125.7, 125.2, 124.4, 122.2, 120.7, 118.9, 117.5, 107.7, 100.9 (aromatic C); 37.5, 34.7, 32.0, 21.7, 21.1, 13.2 (aliphatic C); LC-MS (positive mode): *m/z* = 510 ($M+H^+$); anal. calcd. for $C_{37}H_{35}NO$: C 87.19, H 6.92, N 2.75%; found: C 87.25, H 6.85, N 2.71%.

(2-*tert*-Butyl-5-ethyl-8-pentyl-5*H*-benzo[*b*]carbazol-7-yl)(phenyl)methanone (8g): Yield: 72%; mp 104–106 °C; IR (KBr): ν = 2910, 1720, 1420, 1590, 1060, 850 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.62 (s, 1H), 8.26 (d, *J* = 1.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.62–7.57 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.29–7.27 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.65 (m, 2H), 1.50 (s, 9H), 1.48–1.45 (m, 4H), 1.26 (m, 3H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 201.3, 142.0, 140.7, 140.6, 138.3, 136.7, 134.2, 133.6, 129.9, 129.8, 129.7, 128.7, 126.3, 125.1, 125.0, 124.0, 122.3, 118.8, 117.4, 107.6, 100.6 (aromatic C); 37.5, 34.7, 34.0, 32.0, 31.8, 31.0, 22.4, 13.9, 13.0 (aliphatic C); LC-MS (positive mode): *m/z* = 476 ($M+H^+$); anal. calcd. for $C_{34}H_{37}NO$: C 85.85, H 7.84, N 2.94%; found: C 85.68, H 7.91, N 2.85%.

(2-*tert*-Butyl-5-ethyl-8-hexyl-5*H*-benzo[*b*]carbazol-7-yl)(phenyl)methanone (8h): Yield: 73%; mp 102–104 °C; IR

(KBr): ν = 2915, 1710, 1580, 1110, 650 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 8.61 (s, 1H), 8.25 (d, *J* = 2.0 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.59 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26–7.29 (m, 2H), 4.91 (q, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H), 1.63 (t, *J* = 7.6 Hz, 2H), 1.49–1.47 (m, 11H), 1.24 (m, 7H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 201.3, 142.0, 140.7, 140.6, 138.9, 136.7, 134.2, 133.6, 129.9, 129.7, 129.6, 128.7, 126.2, 125.1, 125.0, 124.0, 122.3, 118.8, 117.4, 107.6, 100.6 (aromatic C); 37.5, 34.7, 34.0, 32.0, 31.5, 31.3, 29.3, 22.5, 14.1, 13.1 (aliphatic C); LC-MS (positive mode): *m/z* = 490 ($M+H^+$); anal. calcd. for $C_{35}H_{39}NO$: C 85.84, H 8.03, N 2.86%; found: C 85.92, H 8.12, N 2.75%.

(2-*tert*-Butyl-5-ethyl-8,9-dipentyl-5*H*-benzo[*b*]carbazol-7-yl)(phenyl)methanone (8i): Yield: 62%; mp 142–144 °C; IR (KBr): ν = 2915, 1720, 1590, 1469, 1060, 850 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.14 (d, *J* = 1.6 Hz, 1H), 7.74 (s, 1H), 7.71 (dd, *J* = 8.8 & 2.0 Hz, 1H), 7.60–7.58 (m, 2H), 7.53 (s, 1H), 7.41–7.20 (m, 14H), 7.00 (t, *J* = 7.2 Hz, 1H), 4.25 (q, *J* = 8.0 Hz, 2H), 1.52 (s, 9H), 1.30 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 200.3, 142.2, 141.2, 141.1, 141.07, 138.4, 137.2, 136.6, 136.4, 133.0, 131.6, 130.3, 129.4, 129.3, 129.0, 128.3, 128.25, 128.1, 127.7, 126.8, 126.4, 126.1, 125.7, 125.2, 122.3, 120.8, 117.0, 107.5, 100.5 (aromatic C); 37.6, 34.8, 32.0, 13.0 (aliphatic C); LC-MS (positive mode): *m/z* = 558 ($M+H^+$); anal. calcd. for $C_{41}H_{35}NO$: C 88.29, H 6.33, N 2.51%; found: C 88.12, H 6.39, N 2.48%.

Phenyl(2,4,5-trimethyl-8,9-diphenyl-5*H*-benzo[*b*]carbazol-7-yl)methanone (8j): Yield: 66%; mp 154–156 °C; IR (KBr): ν = 2910, 1725, 1500, 1600, 1060, 850 cm^{-1}; ^1H NMR (500 MHz, TMS, $CDCl_3$): δ = 8.62 (s, 1H), 8.22 (s, 1H), 8.16 (m, 1H), 7.95 (m, 1H), 7.92 (s, 1H), 7.60 (m, 3H), 7.49 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25–7.15 (m, 8H), 7.11 (s, 1H), 6.74 (t, *J* = 7.0 Hz, 1H), 4.00 (s, 3H), 2.82 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, TMS, $CDCl_3$): δ = 200.7, 142.9, 141.3, 140.6, 138.9, 138.5, 136.4, 135.8, 132.8, 132.2, 131.1, 130.9, 130.1, 129.4, 128.8, 128.7, 128.6, 128.0, 127.6, 127.2, 126.6, 126.2, 125.9, 123.2, 119.9, 119.0, 118.6, 118.1, 100.8 (aromatic C); 32.7, 21.0, 20.1 (aliphatic C); LC-MS (positive mode): *m/z* = 516 ($M+H^+$); anal. calcd. for $C_{38}H_{29}NO$: C 88.51, H 5.67, N 2.72%; found: C 88.39, H 5.63, N 2.81%.

General Procedure for the Synthesis of Carbazolo-[2,3-*b*]carbazole Derivatives

An oven-dried 10-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with 0.5 mmol 9-ethyl-2-(2-phenylethynyl)-9*H*-carbazole-3-carbaldehyde (**6a**), 10 mol% of $Cu(OTf)_2$, and 5 mL of dry 1,2-dichloroethane. To this 0.5 mmol of indole (**9a**) was added. Then the reaction mixture was stirred at 80 °C. After 1 h, solvent was removed under reduced pressure. The crude reaction mixture was then poured over water and extracted with EtOAc (3 × 20 mL). The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed. The residue was purified by column chromatography using silica gel with hexanes-ethyl acetate mixture (eluent: 15% ethyl acetate in hexanes) to afford the product **10a**; yield: 85%. We followed the same procedure for the synthesis of other carbazolo[2,3-*b*]carbazole derivatives **(10b–10l)**.

(8-Ethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)(phenyl)methanone (10a): Yield: 85%; mp 236–238 °C; IR (KBr): ν = 3395, 2950, 1688, 1633, 1555, 1222, 698 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.90 (bs, 1H), 8.90 (s, 1H), 8.73 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.58–7.42 (m, 7H), 7.34–7.24 (m, 3H), 3.95 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.3, 142.8, 142.4, 141.7, 141.5, 140.0, 131.9, 130.7, 129.4, 128.7, 127.3, 127.0, 126.3, 123.7, 123.0, 122.6, 120.8, 120.6, 120.4, 120.3, 119.1, 111.1, 110.8, 108.0, 102.8 (aromatic C); 37.3, 13.1 (aliphatic C); LC-MS (positive mode): *m/z* = 439 ($M+H^+$); anal. calcd. for $C_{31}H_{22}N_2O$: C 84.91, H 5.06, N 6.39%; found: C 84.79, H 5.12, N 6.28%.

(11-*tert*-Butyl-8-ethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)(phenyl)methanone (10b): Yield: 83%; mp 186–188 °C; IR (KBr): ν = 3390, 2978, 1712, 1622, 1545, 1295, 840 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.91 (bs, 1H), 8.92 (s, 1H), 8.77 (s, 1H), 8.27 (d, *J* = 2.0 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.79–7.78 (m, 2H), 7.60–7.41 (m, 7H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.26 (m, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 1.51 (s, 9H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.3, 142.8, 142.2, 143.7, 141.5, 140.5, 140.4, 131.8, 130.6, 129.5, 128.6, 127.2, 126.3, 124.7, 123.6, 123.5, 123.3, 123.0, 122.3, 120.5, 120.2, 117.2, 111.1, 110.8, 107.5, 102.7 (aromatic C); 37.3, 34.7, 32.0, 13.2 (aliphatic C); LC-MS (positive mode): *m/z* = 495 ($M+H^+$); anal. calcd. for $C_{35}H_{30}N_2O$: C 84.99, H 6.11, N 5.66%; found: C 84.91, H 6.15, N 5.58%.

(11-*tert*-Butyl-8-ethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)(*p*-tolyl)methanone (10c): Yield: 86%; mp 180–182 °C; IR (KBr): ν = 3400, 2985, 1675, 1628, 1535, 1295, 700 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.72 (bs, 1H), 8.90 (s, 1H), 8.77 (s, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.58 (dd, *J* = 8.4 & 1.2 Hz, 1H), 7.51–7.40 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.25–7.22 (m, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.49 (s, 9H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.1, 142.6, 142.4, 142.2, 141.7, 140.6, 140.4, 138.6, 130.6, 129.7, 129.3, 127.2, 125.8, 124.6, 123.6, 123.5, 123.3, 123.0, 122.3, 120.5, 120.2, 120.1, 117.2, 111.0, 110.7, 107.4, 102.5 (aromatic C); 37.3, 34.7, 32.0, 21.6, 13.0 (aliphatic C); LC-MS (positive mode): *m/z* = 509 ($M+H^+$); anal. calcd. for $C_{36}H_{32}N_2O$: C 85.01, H 6.34, N 5.51%; found: C 85.15, H 6.29, N 5.63%.

(8-Ethyl-11-methyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)(phenyl)methanone (10d): Yield: 84%; mp 212–214 °C; IR (KBr): ν = 3397, 2980, 1688, 1638, 1527, 1292, 700 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.91 (bs, 1H), 8.88 (s, 1H), 8.69 (s, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.03 (s, 1H), 7.78 (m, 2H), 7.59–7.44 (m, 5H), 7.39 (s, 1H), 7.35–7.31 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.3, 142.8, 141.7, 141.6, 140.6, 140.2, 131.8, 130.7, 129.4, 128.7, 128.4, 128.1, 127.2, 126.3, 123.6, 123.5, 123.0, 122.9, 122.7, 121.0, 120.5, 120.3, 120.25, 111.0, 110.8, 107.7, 102.6 (aromatic C); 37.3, 21.4, 13.1 (aliphatic C); LC-MS (negative mode): *m/z* = 452 (M^+); anal. calcd. for $C_{32}H_{24}N_2O$: C 84.93, H 5.35, N 6.19%; found: C 85.12, H 5.31, N 6.25%.

Phenyl(8,9,11-trimethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)methanone (10e): Yield: 83%; mp 218–220 °C; IR (KBr): ν = 3384, 2987, 1688, 1527, 1292, 700 cm^{-1}; ^1H NMR

(400 MHz, TMS, $CDCl_3$): δ = 9.84 (bs, 1H), 8.87 (s, 1H), 8.63 (s, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.86 (s, 1H), 7.78 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.52–7.44 (m, 4H), 7.34–7.33 (m, 2H), 7.05 (s, 1H), 3.63 (s, 3H), 2.76 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.2, 142.7, 142.2, 141.7, 141.6, 140.1, 131.8, 131.6, 130.3, 129.4, 128.7, 128.6, 127.2, 126.1, 123.7, 123.5, 123.4, 123.0, 120.5, 120.2, 119.7, 119.6, 118.7, 111.1, 110.7, 102.6 (aromatic C); 31.9, 21.1, 20.0 (aliphatic C); LC-MS (negative mode): *m/z* = 452 (M^+); anal. calcd. for $C_{32}H_{24}N_2O$: C 84.93, H 5.35, N 6.19%; found: C 84.85, H 5.31, N 6.25%.

1-(8,9,11-Trimethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)hexan-1-one (10f): Yield: 79%; mp 196–198 °C; IR (KBr): ν = 3387, 2980, 1710, 1527, 1292, 800 cm^{-1}; ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 10.50 (bs, 1H), 8.80 (s, 1H), 8.70 (s, 1H), 8.17 (d, *J* = 7.2 Hz, 1H), 7.95 (s, 1H), 7.89 (s, 1H), 7.46 (m, 2H), 7.29 (m, 1H), 7.10 (s, 1H), 4.13 (s, 3H), 3.38 (m, 2H), 2.85 (s, 3H), 2.55 (s, 3H), 2.01 (m, 2H), 1.42 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 204.9, 143.1, 142.1, 141.7, 140.1, 131.7, 130.0, 128.9, 127.2, 126.3, 123.7, 123.6, 123.4, 122.9, 122.8, 120.6, 120.5, 120.2, 119.8, 118.7, 113.5, 110.8, 100.7 (aromatic C); 44.1, 32.5, 31.8, 25.8, 22.7, 21.1, 20.1, 14.0 (aliphatic C); LC-MS (positive mode): *m/z* = 447 ($M+H^+$); anal. calcd. for $C_{31}H_{30}N_2O$: C 83.37, H 6.77, N 6.27%; found: C 83.25, H 6.71, N 6.35%.

(2-Bromo-8,9,11-trimethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)(phenyl)methanone (10g): Yield: 87%; mp 232–234 °C; IR (KBr): ν = 3399, 2976, 1670, 1537, 1292, 860 cm^{-1}; ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.81 (bs, 1H), 8.77 (s, 1H), 8.59 (s, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 7.86 (s, 1H), 7.76 (m, 2H), 7.55 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.29 (m, 2H), 7.05 (s, 1H), 3.62 (s, 3H), 2.75 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.2, 142.6, 142.4, 141.4, 140.3, 140.1, 131.9, 131.8, 130.8, 129.7, 129.4, 128.8, 128.6, 126.4, 124.9, 123.7, 123.3, 123.2, 122.2, 119.7, 118.7, 112.8, 112.0, 111.3, 102.6 (aromatic C); 31.9, 21.0, 20.0 (aliphatic C); LC-MS (negative mode): *m/z* = 530 (M^+), 532 (M + 2); anal. calcd. for $C_{32}H_{23}BrN_2O$: C 72.32, H 4.36, N 5.27%; found: C 72.45, H 4.41, N 5.18%.

(2-Methoxy-8,9,11-trimethyl-5,8-dihydrocarbazolo[2,3-*b*]-carbazol-6-yl)(phenyl)methanone (10h): Yield: 90%; mp 228–230 °C; IR (KBr): ν = 3388, 2980, 1705, 1638, 1527, 1292, 700 cm^{-1}; ^{1}H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.77 (bs, 1H), 8.80 (s, 1H), 8.60 (s, 1H), 7.85 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.35–7.30 (m, 2H), 7.12 (dd, *J* = 8.4 & 2.4 Hz, 1H), 7.04 (s, 1H), 3.99 (s, 3H), 3.61 (s, 3H), 2.74 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 198.1, 154.5, 143.4, 142.2, 141.7, 136.3, 131.7, 131.6, 130.8, 129.4, 128.7, 128.6, 126.3, 123.6, 123.5, 123.4, 123.3, 122.8, 119.7, 119.6, 118.6, 115.2, 111.3, 110.9, 104.5, 102.6 (aromatic C); 56.2, 31.9, 21.0, 20.0 (aliphatic C); LC-MS (positive mode): *m/z* = 483 ($M+H^+$); anal. calcd. for $C_{33}H_{26}N_2O_2$: C 82.13, H 5.43, N 5.81%; found: C 82.23, H 5.48, N 5.76%.

(2-Hydroxy-8,9,11-trimethyl-5,8-dihydrocarbazolo[2,3-*b*]-carbazol-6-yl)(phenyl)methanone (10i): Yield: 88%; mp 242–244 °C; IR (KBr): ν = 3390, 3300, 2916, 1660, 1638, 1527, 1292, 700 cm^{-1}; ^{1}H NMR (400 MHz, TMS, DMSO-d_6 + $CDCl_3$): δ = 10.73 (s, 1H), 9.12 (s, 1H), 8.95 (s, 1H), 8.82 (s, 1H), 7.89 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.65 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 7.03 (s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 2.71 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, TMS, DMSO-d_6 + $CDCl_3$): δ = 197.6, 151.6, 142.1, 140.5, 140.1, 139.7, 136.5, 133.4, 131.9, 129.9, 129.86, 129.3, 128.4, 124.0, 123.8, 123.2, 122.9, 122.6, 120.2, 120.1, 118.9, 116.2, 112.1, 112.0, 106.4, 100.5 (aromatic C); 32.2, 21.1, 19.9 (aliphatic C); LC-MS (positive mode): *m/z* = 469 ($M+H^+$); anal. calcd. for $C_{32}H_{24}N_2O$: C 82.03, H 5.16, N 5.98%; found: C 82.12, H, 5.22, N 6.07%.

Due to limited solubility, ^{13}C NMR spectra of the following three compounds (**10j**, **10k**, **10l**) could not be taken.

Phenyl(5,8,9,11-tetramethyl-5,8-dihydrocarbazolo[2,3-*b*]-carbazol-6-yl)methanone (10j): Yield: 85%; mp 208–210 °C; IR (KBr): ν = 2970, 1658, 1630, 1505, 1287, 870 cm^{-1}; ^{1}H NMR (500 MHz, TMS, DMSO-d_6): δ = 8.88 (s, 1H), 8.73 (s, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 7.0 Hz, 1H), 7.87 (s, 1H), 7.79 (m, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.49 (m, 2H), 7.33 (s, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 3.89 (s, 3H), 3.55 (s, 3H), 2.78 (s, 3H), 2.50 (s, 3H); LC-MS (positive mode): *m/z* = 467 ($M+H^+$); anal. calcd. for $C_{33}H_{26}N_2O$: C 84.95, H 5.62, N 6.00%; found: C 84.85, H 5.56, N 6.08%.

(2-Fluoro-8,9,11-trimethyl-5,8-dihydrocarbazolo[2,3-*b*]carbazol-6-yl)(phenyl)methanone (10k): Yield: 84%; mp 226–228 °C; IR (KBr): ν = 3405, 2850, 1648, 1610, 1507, 1315, 750 cm^{-1}; ^{1}H NMR (500 MHz, TMS, DMSO-d_6): δ = 11.07 (s, 1H), 9.09 (s, 1H), 8.84 (s, 1H), 8.30 (s, 1H), 8.16 (d, *J* = 7.0 Hz, 1H), 7.95 (s, 1H), 7.77 (dd, *J* = 7.0 & 1.5 Hz, 2H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.54–7.45 (m, 2H), 7.29 (m, 2H), 7.06 (s, 1H), 3.73 (s, 3H), 2.73 (s, 3H), 2.45 (s, 3H); LC-MS (positive mode): *m/z* = 471 ($M+H^+$); anal. calcd. for $C_{32}H_{23}FN_2O$: C 81.68, H 4.93, N 5.95%; found: C 81.52, H 4.89, N 5.88%.

Methyl 6-benzoyl-8,9,11-trimethyl-5,8-dihydrocarbazolo-[2,3-*b*]carbazol-6-yl)carbazole-2-carboxylate (10l): Yield: 74%; mp 234–236 °C; IR (KBr): ν = 3399, 2970, 1710, 1650, 1628, 1507, 1272, 815 cm^{-1}; ^{1}H NMR (500 MHz, TMS, DMSO-d_6): δ = 11.36 (s, 1H), 9.08 (s, 1H), 8.88 (s, 1H), 8.78 (s, 1H), 8.15 (t, *J* = 7.0 Hz, 1H), 7.95–7.49 (m, 7H), 7.27 (s, 1H), 7.02 (s, 1H), 3.94 (s, 3H), 3.74 (s, 3H), 2.74 (s, 3H), 2.45 (s, 3H); LC-MS (negative mode): *m/z* = 486 ($M-H^+$); anal. calcd. for $C_{34}H_{26}N_2O_3$: C 79.98, H 5.13, N 5.49%; found: C 79.85, H 5.21, N 5.56%.

General Procedure for the Synthesis of Indolo[2,3-*b*]-carbazole Derivatives

An oven-dried 10-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with 0.5 mmol of 1-methyl-2-(2-phenylethynyl)-1*H*-indole-3-carbaldehyde (**11b**), 10 mol% of $Cu(OTf)_2$, and 5 mL of dry 1,2-dichloroethane. To this 0.5 mmol of indole (**9a**) was added. Then, the reaction mixture was stirred at 80 °C for 2 h. Then, solvent was removed under reduced pressure. The crude reaction mixture was then poured over water and extracted with EtOAc (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed. The residue was purified by column chromatography using silica gel (eluent: 15% ethyl acetate in hexane). The product **12a** was eluted as a light yellow solid; yield: 31%. We followed the same procedure for the synthesis of the other indolo[2,3-*b*]carbazole derivatives (**12b–12d**)

(5-Methyl-5,7-dihydroindolo[2,3-*b*]carbazol-6-yl)(phenyl)methanone (12a): Yield: 31%; mp 266–268 °C; IR (KBr): ν = 3435, 2968, 1518, 1455, 1010, 805 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$): δ = 9.58 (bs, 1H), 8.90 (s, 1H), 8.21–8.17 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.44–7.39 (m, 5H), 7.34–7.29 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, TMS, $CDCl_3$): δ = 195.6, 142.6, 140.8, 140.2, 139.8, 133.0, 129.5, 125.4, 125.2, 123.8, 123.4, 120.2, 120.0, 119.6, 119.3, 118.7, 118.4, 116.7, 110.8, 109.1, 103.4 (aromatic C); 35.1 (aliphatic C); LC-MS (positive mode): *m/z* = 375 ($M+H^+$); anal. calcd. for $C_{26}H_{18}N_2O$: C 83.40, H 4.85, N 7.48%; found: C 83.31, H 4.81, N 7.56%.

Phenyl{5-(benzenesulfonyl)-5,7-dihydroindolo[2,3-*b*]carbazol-6-yl}methanone (12b): Yield: 42%; mp 254–256 °C; IR (KBr): ν = 3415, 2970, 1718, 1650, 1628, 1537, 1292, 908 cm^{-1}; ^1H NMR (400 MHz, TMS, DMSO-d_6 + $CDCl_3$): δ = 10.80 (s, 1H), 8.60 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.90 (m, 1H), 7.82 (m, 1H), 7.66–7.60 (m, 4H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.39–7.31 (m, 4H), 7.20 (m, 2H), 7.00–6.95 (m, 4H); ^{13}C NMR (100 MHz, TMS, DMSO-d_6 + $CDCl_3$): δ = 193.3, 141.2, 139.6, 139.1, 138.1, 135.4, 134.4, 133.4, 132.1, 129.3, 129.1, 128.0, 127.9, 126.3, 125.9, 125.5, 123.2, 121.7, 121.5, 119.8, 119.5, 119.1, 117.9, 114.1, 111.8, 111.2, 110.7 (aromatic C); LC-MS (positive mode): *m/z* = 501 ($M+H^+$); anal. calcd. for $C_{31}H_{20}N_2O_3S$: C 74.38, H 4.03, N 5.60%; found: C 74.26, H 4.10, N 5.52%.

{2-Hydroxy-7-(benzenesulfonyl)-5,7-dihydroindolo[2,3-*b*]carbazol-6-yl}(phenyl)methanone (12c): Yield: 48%; mp 242–244 °C; IR (KBr): ν = 3418, 3320, 2990, 1728, 1670, 1638, 1437, 1382, 710 cm^{-1}; ^1H NMR (400 MHz, TMS, DMSO-d_6): δ = 11.15 (s, 1H), 9.17 (bs, 1H), 8.92 (s, 1H), 8.31 (s, 1H), 8.05–7.93 (m, 2H), 7.62–7.43 (m, 9H), 7.17–6.97 (m, 5H); ^{13}C NMR (100 MHz, TMS, DMSO-d_6): δ = 193.2, 151.8, 151.8, 139.8, 138.5, 135.7, 135.5, 134.7, 133.1, 129.7, 129.3, 129.1, 128.9, 126.7, 126.4, 123.6, 122.9, 121.1, 120.2, 119.7, 118.3, 116.6, 115.6, 113.2, 112.7, 111.5, 105.4 (aromatic C); LC-MS (negative mode): *m/z* = 515 ($M-H^+$); anal. calcd. for $C_{31}H_{20}N_2O_4S$: C 72.08, H 3.90, N 5.42%; found: C 72.15, H 3.95, N 5.36%.

Methyl 6-benzoyl-7-(benzenesulfonyl)-5,7-dihydroindolo-[2,3-*b*]carbazol-6-yl)carbazole-2-carboxylate (12d): Yield: 39%; mp 248–250 °C; IR (KBr): ν = 3433, 2890, 1738, 1722, 1612, 1427, 1282, 708 cm^{-1}; ^1H NMR (400 MHz, TMS, DMSO-d_6): δ = 11.84 (s, 1H), 9.26 (s, 1H), 8.95 (s, 1H), 8.09–8.05 (m, 2H), 7.96–7.93 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.49–7.42 (m, 4H), 7.19 (t, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, TMS, DMSO-d_6): δ = 192.9, 167.2, 144.7, 139.8, 139.7, 138.2, 135.9, 134.9, 134.6, 133.3, 129.7, 129.4, 129.3, 129.0, 128.0, 127.3, 126.7, 126.5, 123.4, 123.1, 122.7, 122.1, 121.4, 120.4, 118.2, 116.2, 112.4, 112.3 (aromatic C); 52.4 (aliphatic C); LC-MS (negative mode): *m/z* = 557 ($M-H^+$); anal. calcd. for $C_{33}H_{22}N_2O_5S$: C 70.95, H 3.97, N 5.01%; found: C 70.89, H 3.91, N 5.10%.

Procedure for the Synthesis of 6-Ethyl-1,6-dihydro-1-(1*H*-indol-3-yl)-9-methyl-3-phenylpyrano[4,3-*b*]carbazole (13)

An oven-dried 10-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with 0.5 mmol of 9-ethyl-6-methyl-2-(2-phenylethynyl)-9*H*-carbazole-3-carbaldehyde (**6b**), 10 mol% of $PdCl_2$, and 5 mL of DMSO. To this 0.5 mmol of indole (**9a**) was added. Then, the reaction mixture was stirred at room temperature. After completion of the reaction as monitored by TLC, the crude reaction mixture was poured over water and extracted with dichloromethane (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography using silica gel (eluent: 20% ethyl acetate in hexanes). The product **13** was eluted as a viscous liquid; yield: 78%. IR (neat): ν = 3056, 2965, 2912, 1457, 1045, 1035, 769 cm^{-1}; ^1H NMR (500 MHz, TMS, $CDCl_3$): δ = 8.03 (bs, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.71–7.69 (m, 3H), 7.66 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.29–7.28 (m, 3H), 7.27 (s, 1H), 7.23–7.20 (m, 2H), 7.18–7.16 (m, 2H), 6.87 (s, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.67 (s, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 2.46 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, TMS, $CDCl_3$): δ = 152.3, 140.4, 138.5, 136.6, 135.1, 130.3, 128.4, 128.2, 128.1, 126.7, 126.5, 125.3, 125.0, 123.4, 122.3, 122.2, 121.2, 120.3, 120.1, 120.0, 117.1, 116.4, 111.2, 108.1, 103.2, 102.0 (aromatic C); 74.8, 37.7, 21.3, 13.9 (aliphatic C); LC-MS (negative mode): *m/z* = 453 ($M-H^+$), 454 (M^+); anal. calcd. for $C_{32}H_{26}N_2O$: C 84.55, H 5.77, N 6.16%; found: C 84.41, H 5.71, N 6.25%.

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