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$Cu(OTf)_2$/HFIP catalyzed regioselective cycloisomerization of indole-C3-functionalized alkynols to carbazoles†

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We report here a simple and atom economic cycloisomerization reaction of indole-tethered alkynols for constructing diverse carbazoles using $Cu(OTf)_2$/HFIP as the excellent promoter system. The reaction proceeds through a one-pot, domino process of spiro cyclization and 1,2-migration followed by aromatization to deliver carbazoles.

Introduction

Carbazole structural frameworks have received overwhelming attention from the scientific community due to their rich natural abundance and broad range of biological activities such as anticancer, antipsychotic, antibiotic, anti-inflammatory, antioxidative, and antimicrobial activities (Fig. 1).[1] Moreover, carbazole templates serve as useful platforms for the design of new organic materials because of their efficiency in hole-transporting and their light-emitting and photoconductive properties.[2] Therefore, the development of efficient and economical synthetic methods for carbazoles continues to be a desirable task in organic synthesis.[3] Despite several classical and elegant synthetic methods, the benzannulation of a C-2 or a C-3 alkyne tethered indole moiety is considered as one of the most accessible means for synthesizing carbazoles due to its efficient conversion and atom economy;[4–7] most of these methods are catalyzed by platinum,[4] gold,[5] or silver complexes.[6] In particular, the annulation of C3-alkynol tethered indoles becomes more interesting for the construction of carbazoles *via* spiro-cyclization. Based upon the nature of substitutions, electronic and steric effects, and also the carbon chain length, they undergo either an *endo*- or *exo*-cyclization to form intermediate **X**, as shown in Fig. 2.[8] Subsequently, the spirane intermediate can undergo a 1,2-alkenyl migration[9] to form carbazole **Y** or carbazole **Z** *via* 1,2-alkyl migration.[10] For example, the Min Shi group developed an intramolecular cyclization of 1-(indol-3-yl)-3-alkyn-1-ols (alcohol being on the *a*-carbon) in the presence of a cationic gold(I) complex to form a substituted carbazole through a 1,2-alkyl migration and aromatization (Fig. 2, eqn (i)).[11] The Unsworth group developed an Ag(OTf) mediated carbazole synthesis from indole-C3-tethered propargyl alcohols (alcohol being on the *b*-carbon, Fig. 2, eqn (ii)).[12] Next, a detailed study on a 1,2-migration of a gold(III)-catalyzed cycloisomerization of α-bis(indol-3-yl)methyl alkynols to afford 1-(indol-3-yl)carbazoles was reported by the R. Sanz group.[13] Baire's group reported a silver triflate-mediated cycloisomerization of (indol-3-yl)pentyn-3-ols to produce tetrahydrocarbazoles, which underwent a dehydrative aromatization to form carbazoles in the presence of *p*TSA.[14] In continuation of our research aimed at developing nitrogen heterocycles[15] from propargyl alcohols, recently, we developed an iodo-cycloisomerization of indole-tethered propargylic alcohols to furnish 3-iodocarbazoles *via* selective 1,2-alkyl migration[8b] and 2-iodocarbazoles *via* 1,2-alkenyl migration.[8c] Though elegant approaches are available, there is still a need to develop a sustainable method that avoids excess solvents, inert conditions and expensive catalysts.

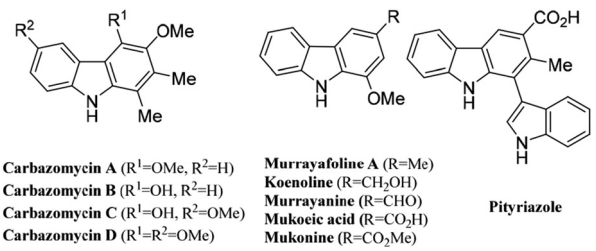

Fig. 1 Selected examples of functionalized, biologically active carbazole natural products.

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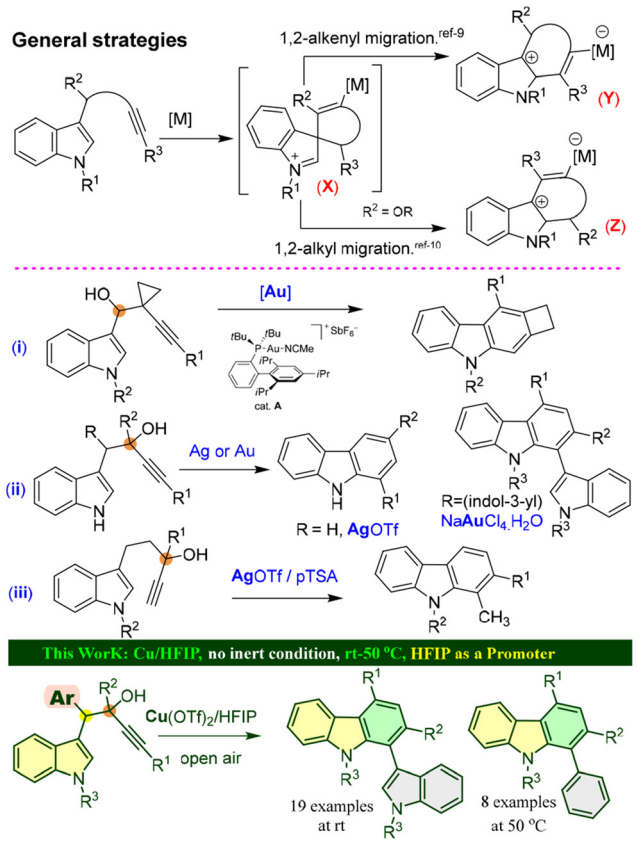


Fig. 2 Selected examples of cycloisomerization of indoles bearing C3-alkynols toward carbazoles.

Table 1 Optimization of reaction conditions[a]

Entry	Reaction conditions[a]	Yield[b] (%)
1	*p*TSA (10), DCE, 25 °C, 24 h	10
2	TfOH (10), DCE, 25 °C, 4 h	—[c]
3	$MeSO_3H$ (10), DCE, 25 °C, 4 h	—[c]
4	$HNTf_2$ (10), DCE, 25 °C, 4 h	—[c]
5	$BF_3{\cdot}Et_2O$ (10), DCE, 25 °C, 4 h	—[c]
6	$Ca(NTf_2)_2/Bu_4NPF_6$ (10), DCE, 25 °C, 8 h	12
7	$Mg(OTf)_2$ (10), DCE, 25 °C, 24 h	nr
8	$FeCl_3$ (10), DCE, 25 °C, 24 h	nr
9	$Cu(OTf)_2$ (10), DCE, 25 °C, 4 h	43
10	$Cu(OTf)_2$ (10), toluene, 25 °C, 1 h	45
11	$Cu(OTf)_2$ (10), DMSO, 25 °C, 24 h	nr
12	$Cu(OTf)_2$ (10), CH_3CN, 25 °C, 2 h	25
13	$Cu(OTf)_2$ (10), HFIP, 25 °C, 15 min	82
14[d]	**$Cu(OTf)_2$ (10), HFIP (0.2 mL), 25 °C, 15 min**	**96**
15	HFIP, 25 °C, 24 h	nr
16	$Cu(OTf)_2$ (10), MeOH, 25 °C, 6 h	43
17	$Cu(OTf)_2$ (10), EtOH, 25 °C, 6 h	48
18	$Cu(OTf)_2$ (10), H_2O, 25 °C, 24 h	nr
19	$Cu(OTf)_2$ (10), MeOH/DCE, 25 °C, 4 h	54
20	$Cu(OTf)_2$ (10), MeOH/CH_3CN, 25 °C, 8 h	50
21	$Cu(OAc)_2$ (10), HFIP, 25 °C, 4 h	60
22	CuI (10), HFIP, 25 °C, 24 h	nr

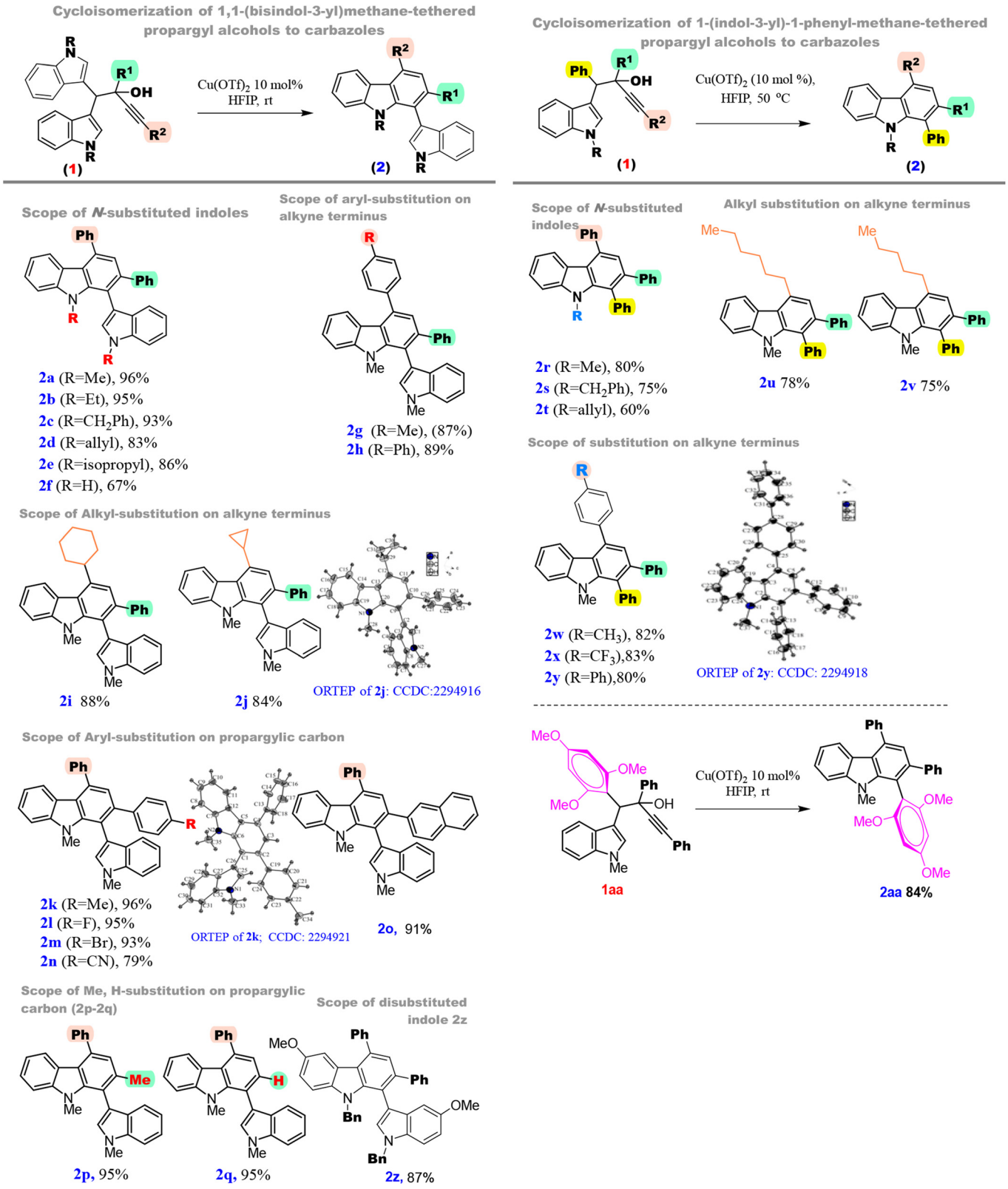
[a] Unless mentioned, all the reactions were carried out with **1a** (100 mg) in 2 mL solvent at rt under specified conditions. [b] Isolated yields. [c] Complex TLC. [d] Optimum conditions. nr = no reaction.

Results and discussion

In continuation of our pursuit to study and understand aryl migrations during 1,2-shifts of indole-tethered propargyl alcohols to furnish carbazoles,[8b,c] we chose compound **1a** as the model substrate. Therefore, we commenced our study by treating **1a** with 10 mol% *p*TSA in 1,2-dichloromethane (DCE) at room temperature; after 24 h, we isolated the desired product **2a** in 10% yield (entry 1, Table 1). Encouraged by this observation, we then screened some more Brønsted acids, such as triflic acid (entry 2), methanesulfonic acid (entry 3) and triflimide (entry 4) in DCE at rt. All these reactions led to the formation of a complex TLC along with a trace of **2a**. Next, we switched to Lewis acid catalysts, like $BF_3{\cdot}Et_2O$ (entry 5), $Ca(NTf_2)_2$ (entry 6) and $Mg(OTf)_2$ (entry 7) and found only $Ca(NTf_2)_2$ catalyzed the reaction for the formation of **2a** in 12% yield. Then, we performed the reaction with Earth-abundant transition metal catalysts; $FeCl_3$ did not catalyze the reaction, but $Cu(OTf)_2$ furnished **2a** in 43% yield. With this, we identified $Cu(OTf)_2$ as the right catalyst and started screening various solvents. 45% **2a** was formed in toluene, but no product was observed in DMSO, and acetonitrile gave only 25% product yield. In recent years, HFIP showed excellent results in catalysis; therefore,[16] we used HFIP as the solvent (2 mL) in our reaction, and to our surprise, HFIP/$Cu(OTf)_2$ promoted the formation of **2a** in 82% yield at rt (entry 13). When we used 2 equiv. of HFIP (twice the total weight of **1a** + catalyst), *i.e.* 0.2 mL, a quantitative yield of **2a** (96%) was observed. Looking at the sharp rise in the reaction yield due to HFIP, we were curious to know if the catalyst is really required for this transformation. Therefore, we stirred **1a** with only HFIP and found that no reaction was initiated, which confirms the role of HFIP. Further attempts with protic solvents (methanol, ethanol, water) and mixed solvents (MeOH/DCE, MeOH/CH_3CN) were not encouraging (entries 16–20). Copper acetate was catalysed to furnish a moderate yield of **2a** (entry 21), but no reaction occurred with copper iodide (entry 21). Finally, we concluded that 10 mol% $Cu(OTf)_2$ and HFIP (0.2 mL) at rt were the best reaction conditions for the cycloisomerization (entry 14, Table 1).

With the optimum reaction conditions in hand, we were keen to check the generality of the protocol (Table 2). Initially, we studied the scope of *N*-substituted indoles with methyl, ethyl, benzyl, allyl, and isopropyl groups; all reacted smoothly to yield corresponding carbazoles **2a–2e** in excellent yields. However, it was observed that N–H indoles gave moderate yields when compared to *N*-alkyl indoles. Next, we noticed that *p*-tolyl and *p*-biphenyl substitutions on the alkyne terminus also furnished carbazoles **2g** and **2h** in excellent yields.

Table 2 Substrate scope[a]



[a] All the reactions were performed with 100 mg of propargyl alcohol (1) in 0.2 mL of HFIP.

Moreover, substrates bearing cyclohexyl and cyclopropyl groups on the alkyne terminus reacted smoothly to furnish **2i** and **2j**. Single crystal-X-ray data of **2j** were obtained to understand the regioselectivity of this protocol. Next, we focussed on understanding the electronic effects on the phenyl ring at the propargylic carbon. The benzene ring bearing, methyl, fluoro, and bromo substitutions at the *para* position showed quantitative yields of carbazoles **2k–2m**. However, the yield in the case of *p*-cyanobenzene was slightly lower due to the strong-I effect (**2n**). We have also obtained the single crystal X-ray data of **2k** to understand the regioselectivity of the protocol. Besides, we were quite successful in demonstrating the reactivity of substrates having 2-naphthyl, methyl and hydrogen (a secondary propargylic system) substitutions at the propargylic carbon to synthesize carbazoles **2o–2q** in excellent yields. Motivated by this outcome, with bis(indolyl) systems, we intended to study the indole-phenyl tethered propargylic alcohols. Accordingly, we subjected compound **1r** to the standard reaction conditions, and gratifyingly, the reaction gave the desired product **2r** but in a lower yield. Yet, we circumvented this issue by performing the reaction at 50 °C and obtained **2r** in 80% yield. Furthermore, we found that *N*-Me, *N*-benzyl and *N*-allyl derivatives of indoles also reacted smoothly at 50 °C to furnish the desired carbazoles **2r–2t** in good yields. *N*-Hexyl and *n*-pentyl substituted alkynols (**1u** and **1v**) also showed excellent reactivity to furnish **2u** and **2v**. Similarly, *p*-phenyl substituted benzene on an alkyne terminus was also shown to produce **2w–2y** in good yields. Single-crystal-X-ray data of **2y** were obtained. Carbazole **2z** was synthesized in 87% yield from the 5-methoxyindole derivative **1z**. Interestingly, 1,3,5-trimethoxy benzene substitution was also well tolerated under the standard conditions to furnish the desired carbazole **2aa** in 84% yield.

From the reaction screening (Table 1), it was clear that HFIP alone could not initiate the reaction, and $Cu(OTf)_2$ without HFIP furnished a poor yield of **2a**. Based on these observations and previous reports,[16] we believe that HFIP activates both the catalyst and substrate through hydrogen bonding, as depicted in Fig. 3. The Cu/HFIP activates the substrate *via* the classical formation of a *p*-Lewis acid complex (**A**), which undergoes a 5-*endo-dig* spirocyclization to form the spirane **B**. A subsequent 1,2-alkyl migration of the spirane forms intermediate **C**, and the subsequent protodemetallation and aromatization furnishes the desired carbazole **2**.

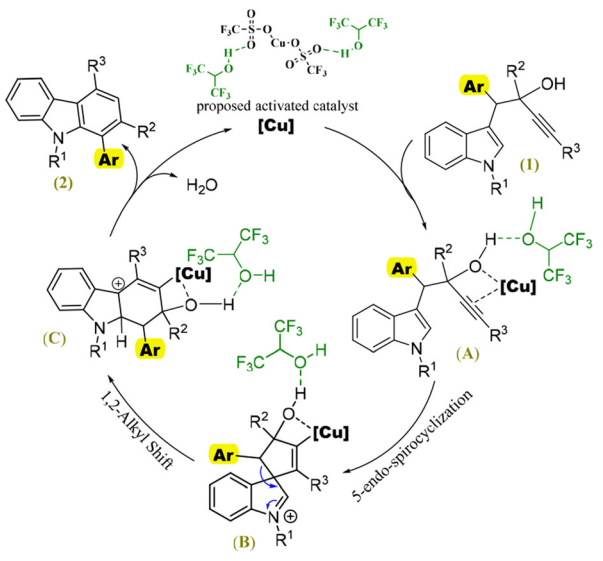


Fig. 3 Proposed reaction mechanism.

Conclusions

In conclusion, we have developed a simple, operationally friendly protocol for the annulation of indole-C3-attached propargyl alcohols to construct functionally diverse carbazoles. The reaction was performed using catalytic $Cu(OTf)_2$ and HFIP at rt for bisindolyl (**2a–2q** and **2z**) and indolyl-trimethoxybenzene (**2aa**) systems in open air. The indole-phenyl system required moderate heating (**2r–2y**). Furthermore, this protocol does not require inert conditions and solvent media. Broad substrate scope, high yields, and open-air reactions using a minimum amount of HFIP are the key highlights of our method.

Experimental

General information

Unless otherwise noted, all reagents were used as received from commercial suppliers, and indenols were synthesized by following the reported procedures. Reactions were performed in flame-dried or oven-dried glassware with magnetic stirring and were monitored using thin-layer chromatography (TLC) with aluminum sheets of silica gel 60 F_{254} from Merck. TLC plates were visualized with UV light (254 nm), iodine treatment, or using *p*-anisaldehyde or vanillin stain. Column chromatography was carried out using silica gel 60–120 and 100–200 mesh size as the stationary phase. NMR spectra were recorded at 500 MHz and 400 MHz (^1H) and 125 MHz and 100 MHz ($^{13}C\{^1H\}$), respectively, on a Bruker Avance spectrometer. NMR spectra were solved by using the Bruker Topspin software. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (^1H: δ = 7.26 and $^{13}C\{^1H\}$: δ = 77.16 ppm) as the internal standard, and coupling constants (J) are given in Hz. HRMS were recorded using ESI-TOF techniques. Melting points were measured with LABINDIA's melting point apparatus (MEPA).

General experimental procedure for the synthesis of carbazole 2. Alkynol **1** (100 mg, 1 equiv.), HFIP (0.2 mL) and 10 mol% $Cu(OTf)_2$ were weighed into a small round bottom flask equipped with a tiny magnetic bead and stirred slowly at room temperature. The reaction mixture turned reddish immediately after the addition of HFIP. Slow stirring is required to avoid the spilling of the reaction mixture onto the walls of the reaction flask (see the ESI for more details†). The reaction progress was

monitored by TLC. After the completion of the reaction, the crude compound was absorbed into silica gel and purified by column chromatography on silica gel using a mixture of hexane and AcOEt as eluents to obtain carbazole **2**.

*9-Methyl-1-(1-methyl-1H-indol-3-yl)-2,4-diphenyl-9H-carbazole (**2a**).* Isolated as a pale yellow solid; yield: 96% (0.092 g); mp: 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.0 Hz, 2H), 7.49–7.46 (m, 2H), 7.38–7.35 (m, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.26–7.22 (m, 2H), 7.19 (s, 1H), 7.15–7.13 (m, 2H), 7.08–7.05 (m, 4H), 6.97 (t, J = 7.5 Hz, 1H), 6.70 (s, 1H), 3.72 (s, 3H), 3.25 (s, 3H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.9, 141.8, 141.5, 140.9, 136.5, 136.3, 131.2, 129.7, 129.5, 129.4, 128.5, 127.6, 127.3, 125.9, 125.5, 123.6, 122.3, 121.8, 120.5, 120.4, 119.8, 118.7, 115.2, 112.0, 109.2, 108.8, 32.9, 31.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{34}H_{27}N_2$ $[M + H]^+$ 463.2174, found 463.2177.

*9-Ethyl-1-(1-ethyl-1H-indol-3-yl)-2,4-diphenyl-9H-carbazole (**2b**).* Isolated as a pale yellow solid; yield: 95% (0.091 g); mp: 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.48–7.46 (m, 2H), 7.37–7.37 (m, 3H), 7.29 (d, J = 7.0 Hz, 1H), 7.23 (t, J = 3.5 Hz, 1H), 7.21–7.19 (m, 1H), 7.11–7.10 (m, 2H), 7.06–7.02 (m, 4H), 6.96 (t, J = 7.5 Hz, 1H), 6.79 (s, 1H), 4.14–4.03 (m, 2H), 3.93–3.85 (m, 1H), 3.84–3.77 (m, 1H), 1.26 (t, J = 7.0 Hz, 3H), 0.86 (t, J = 6.5 Hz, 3H) ppm; ^{13}C{1H} (125 MHz, $CDCl_3$) δ 143.0, 142.1, 141.8, 141.5, 139.8, 136.5, 135.1, 131.2, 129.6, 129.5, 128.5, 127.5, 127.4, 127.1, 125.8, 125.4, 123.4, 122.8, 122.5, 121.7, 120.8, 120.5, 119.6, 118.7, 115.2, 112.0, 109.4, 109.1, 40.9, 38.4, 15.8, 14.3 ppm; HRMS (ESI-TOF): m/z calculated for $C_{36}H_{31}N_2$ $[M + H]^+$ 491.2487, found 491.2487.

*9-Benzyl-1-(1-benzyl-1H-indol-3-yl)-2,4-diphenyl-9H-carbazole (**2c**).* Isolated as a white solid; yield: 93% (0.090 g); mp: 174–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 7.0 Hz, 2H), 7.53–7.48 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.32–7.28 (m, 1H), 7.24–7.22 (m,1H), 7.21 (d, J = 7.5 Hz, 1H), 7.17–7.15 (m, 3H), 7.14–7.13 (m, 3H), 7.12–7.09 (m, 3H), 7.06–6.97 (m, 6H), 6.61–6.59 (m, 2H), 6.51–6.49 (m, 2H), 6.23 (s, 1H), 5.12–5.02 (m, 3H), 4.69–4.65 (m, 1H) ppm; ^{13}C {1H}(100 MHz, $CDCl_3$) δ 176.1, 164.3, 161.8, 151.4, 149.2, 130.9, 129.2, 127.9, 127.8, 127.4, 127.0, 126.6, 124.9, 121.9, 120.0, 116.3, 116.1, 112.6, 49.5, 31.2, 19.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{46}H_{35}N_2$ $[M + H]^+$ 615.2800, found 615.2790.

*9-Allyl-1-(1-allyl-1H-indol-3-yl)-2,4-diphenyl-9H-carbazole (**2d**).* Isolated as a white solid; yield: 83% (0.080 g); mp: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.72 (m, 2H), 7.54 (t, J = 7.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.35–7.32 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 7.25–7.21 (m, 1H), 7.20–7.19 (m, 2H), 7.16–7.14 (m, 2H), 7.05–7.02 (m, 4H), 6.97 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 1.0 Hz, 1H), 5.86–5.79 (m, 1H), 5.50–5.42 (m, 1H), 5.05 (d, J = 10.5 Hz, 1H), 4.85 (d, J = 10.0 Hz, 1H), 4.72–4.66 (m, 2H), 4.63–4.57 (m, 2H), 4.45–4.35 (m, 2H) ppm; ^{13}C{1H} NMR (125 MHz, $CDCl_3$): δ 142.8, 142.2, 141.4, 140.1, 136.5, 135.5, 133.7, 133.2, 130.7, 129.6, 129.5, 128.5, 128.4, 127.6, 127.2, 125.9, 125.4, 123.6, 122.6, 122.3, 121.9, 120.6, 119.8, 119.0, 116.6, 115.5, 115.1, 111.8, 48.4, 46.3 ppm; HRMS (ESI-TOF): m/z calculated for $C_{38}H_{31}N_2$ $[M + H]^+$ 515.2487, found 515.2487.

*9-Isopropyl-1-(1-isopropyl-1H-indol-3-yl)-2,4-diphenyl-9H-carbazole (**2e**).* Isolated as a yellowish solid; yield: 86% (0.083 g); mp: 199–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 8.5 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.49–7.45 (m, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.37–7.33 (m, 2H), 7.30–7.27 (m, 1H), 7.21–7.18 (m, 1H), 7.16 (s, 1H), 7.08–7.06 (m, 2H), 7.03–6.99 (m, 4H), 6.94–6.91 (m, 1H), 6.84 (s, 1H), 4.96–4.90 (m, 1H), 4.64–4.59 (m, 1H), 1.46 (d, J = 6.5 Hz, 3H), 1.24–1.20 (m, 6H), 1.14 (d, J = 7.0 Hz, 3H) ppm; ^{13}C{1H} NMR (125 MHz, $CDCl_3$): δ 143.2, 142.3, 141.6, 140.4, 140.3, 136.2, 135.3, 130.0, 129.5, 128.5, 127.5, 127.0, 125.7, 124.6, 123.8, 123.3, 122.6, 121.6, 120.9, 120.6, 119.4, 118.3, 115.6, 112.7, 112.6, 109.3, 46.9, 46.5, 22.9, 22.8, 21.0, 20.0 ppm; HRMS (ESI-TOF): m/z calculated for $C_{38}H_{31}N_2$ $[M + H]^+$ 519.2800, found 519.2805.

*1-(1H-Indol-3-yl)-2,4-diphenyl-9H-carbazole (**2f**).* Isolated as a brown viscous compound; yield: 67% (0.064 g); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.13 (s, 1H), 7.77 (d, J = 7.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.0 Hz, 2H), 7.50–7.46 (m, 3H), 7.32–7.27 (m, 6H), 7.17–7.12 (m, 4H), 7.00–6.97 (m, 1H), 6.88 (d, J = 2.0 Hz, 1H) ppm; ^{13}C{1H} NMR (125 MHz, $CDCl_3$): δ 142.2, 141.2, 140.2, 140.0, 139.3, 136.5, 136.2, 130.0, 129.4, 128.5, 127.7, 127.6, 127.1, 126.3, 125.6, 124.8, 123.8, 123.2, 122.5, 120.4, 120.2, 119.6, 119.1, 114.9, 112.2, 111.6, 110.6 ppm; HRMS (ESI-TOF): m/z calculated for $C_{32}H_{23}N_2$ $[M + H]^+$ 435.1861, found 435.1867.

*9-Methyl-1-(1-methyl-1H-indol-3-yl)-2-phenyl-4-(p-tolyl)-9H-carbazole (**2g**).* Isolated as a white solid; yield: 87% (0.084 g); mp: 223–224 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.49–7.46 (m, 2H), 7.37–7.34 (m, 3H), 7.27 (s, 1H), 7.24 (s, 1H), 7.17 (s, 1H), 7.09–7.06 (m, 1H), 7.04 (d, J = 7.5 Hz, 2H), 6.98–6.95 (m, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.73 (s, 1H), 3.75 (s, 3H), 3.23 (s, 3H), 2.22 (s, 3H) ppm; ^{13}C{1H}(125 MHz, $CDCl_3$) δ 176.1, 151.4, 150.4, 132.2, 131.2, 130.1, 129.2 (2), 129.1, 129.0, 125.8 (2), 125.4, 123.6, 120.3, 118.5, 116.7, 113.7, 49.4, 31.2, 19.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{35}H_{29}N_2$ $[M + H]^+$ 477.2331, found 477.2330.

*4-([1,1'-Biphenyl]-4-yl)-9-methyl-1-(1-methyl-1H-indol-3-yl)-2-phenyl-9H-carbazole (**2h**).* Isolated as a white solid; yield: 89% (0.086 g); mp: 225–226 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.77 (m, 4H), 7.75 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.40–7.36 (m, 3H), 7.33 (d, J = 8.5 Hz, 1H), 7.27–7.23 (m, 3H), 7.16–7.15 (m, 2H), 7.08–7.06 (m, 4H), 7.01–6.98 (m, 1H), 6.71 (s, 1H), 3.72 (s, 3H), 3.27 (s, 3H) ppm; ^{13}C{1H}(100 MHz, $CDCl_3$) δ 142.9, 141.9, 141.0, 140.5, 140.3, 136.3, 136.0, 131.2, 129.9, 129.7, 129.4, 128.9, 127.4, 127.3, 127.2 (2), 126.0, 125.5, 123.6, 122.4, 122.3, 121.8, 120.5, 120.3, 119.8, 118.8, 115.3, 112.0, 109.2, 108.8, 32.9, 31.5 ppm; HRMS (ESI-TOF): m/z calculated for $C_{40}H_{31}N_2$ $[M + H]^+$ 539.2487, found 539.2481.

*4-Cyclohexyl-9-methyl-1-(1-methyl-1H-indol-3-yl)-2-phenyl-9H-carbazole (**2i**).* Isolated as a white solid; yield: 88% (0.085 g); mp: 220–221 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 7.5 Hz, 1H), 7.45–7.42 (m, 1), 7.31 (d, J = 3.5 Hz, 1H), 7.29–7.27 (m, 3H), 7.23–7.20 (m, 1H), 7.19 (s, 1H), 7.13–7.11 (m, 2H),

7.08–7.06 (m, 3H), 7.04–7.01 (m, 1H), 6.64 (s, 1H), 3.70 (s, 3H), 3.66–3.56 (m, 1H), 3.22 (s, 3H), 2.31–2.28 (m, 2H), 1.99 (s, 2H), 1.89 (d, J = 7.5 Hz, 1H), 1.72–1.63 (m, 4H), 1.43–1.36 (m, 1H) ppm; ^{13}C{1H}(100 MHz, $CDCl_3$) δ 143.6, 142.8, 142.3, 142.1, 140.8, 136.3, 131.2, 129.7, 129.4, 127.2, 125.8, 124.9, 122.7, 122.4, 121.6, 120.6, 120.4, 119.6, 119.1, 118.5, 113.6, 112.3, 109.1, 108.8, 41.0, 33.3, 33.2, 32.9, 31.4, 27.5, 27.4, 26.7 ppm; HRMS (ESI-TOF): m/z calculated for $C_{34}H_{33}N_2$ $[M + H]^+$ 469.2644, found 469.2648.

*4-Cyclopropyl-9-methyl-1-(1-methyl-1H-indol-3-yl)-2-phenyl-9H-carbazole (**2j**).* Isolated as a yellowish solid; yield: 84% (0.081 g); mp: 246–247 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 8.56 (d, J = 7.5 Hz, 1H), 7.48–7.44 (m, 1H), 7.32–7.29 (m, 3H), 7.28–7.26 (m, 1H), 7.23–7.20 (m, 1H), 7.11–7.09 (m, 2H), 7.08–7.05 (m, 4H), 7.04–7.01 (m, 1H), 6.64 (s, 1H), 3.70 (s, 3H), 3.23 (s, 3H), 2.67–2.62 (m, 1H), 1.20–1.17 (m, 2H), 1.00–0.96 (m, 2H) ppm; ^{13}C{1H}(125 MHz, $CDCl_3$) δ (ppm) 143.3, 142.7, 141.8, 140.6, 136.6, 136.3, 131.2, 129.6, 129.4, 127.2, 125.8, 125.1, 123.1, 123.0, 122.5, 121.7, 120.5, 120.3, 119.7, 119.0, 114.1, 112.1, 109.1, 108.6, 32.9, 31.3, 15.0, 6.9 (2) ppm; HRMS (ESI-TOF): m/z calculated for $C_{31}H_{27}N_2$ $[M + H]^+$ 427.2174, found 427.2175.

*9-Methyl-1-(1-methyl-1H-indol-3-yl)-4-phenyl-2-(p-tolyl)-9H-carbazole (**2k**).* Isolated as a white solid; yield: 96% (0.093 g); mp: 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.47 (d, J = 7.5 Hz, 2H), 7.37–7.32 (m, 3H), 7.25–7.22 (m, 2H), 7.17 (s, 1H), 7.08–7.03 (m, 3H), 6.96 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.5 Hz, 2H), 6.71 (s, 1H), 3.72 (s, 3H), 3.22 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C{1H}(100 MHz, $CDCl_3$) δ 142.9, 141.8, 141.5, 141.0, 139.9, 136.4, 136.3, 135.4, 131.3, 129.5, 129.3, 128.5, 128.0, 127.5, 125.4, 123.7, 122.3, 121.7, 120.5, 120.2, 119.8, 118.7, 115.1, 112.1, 109.2, 108.7, 32.9, 31.4, 21.1 ppm; HRMS (ESI-TOF): m/z calculated for $C_{35}H_{29}N_2$ $[M + H]^+$ 477.2331, found 477.2329.

*2-(4-Fluorophenyl)-9-methyl-1-(1-methyl-1H-indol-3-yl)-4-phenyl-9H-carbazole (**2l**).* Isolated as a pale yellow solid; yield: 95% (0.092 g); mp: 234–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.55–7.52 (m, 2H), 7.50–7.45 (m, 2H), 7.38–7.33 (m, 3H), 7.26–7.23 (m, 3H), 7.14 (s, 1H), 7.11–7.05 (m, 3H), 6.99–6.95 (m, 1H), 6.76–6.72 (m, 2H), 6.71 (s, 1H), 3.75 (s, 3H), 3.25 (s, 3H) ppm; ^{13}C{1H}(100 MHz, $CDCl_3$) δ 162.7, 160.2, 142.9, 141.3, 140.9, 140.7, 138.8, 136.5, 136.3, 131.1, 131.0, 129.4, 129.3, 128.5, 127.6, 125.5, 123.4, 122.3, 122.2, 121.9, 120.5, 120.4, 119.9, 118.8, 115.2, 114.2, 114.0, 111.9, 109.3, 108.8, 33.0, 31.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{34}H_{26}FN_2$ $[M + H]^+$ 481.2080, found 481.2076.

*2-(4-Bromophenyl)-9-methyl-1-(1-methyl-1H-indol-3-yl)-4-phenyl-9H-carbazole (**2m**).* Isolated as a white solid; yield: 93% (0.090 g); mp: 200–201 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.55–7.52 (m, 2H), 7.50–7.48 (m, 1H), 7.46 (d, J = 8.0 Hz, 1H), 3.84 (s, 3H), 7.38–7.32 (m, 3H), 7.25 (t, J = 9.0 Hz, 2H), 7.18–7.16 (m, 2H), 7.12 (s, 1H), 7.09–7.05 (m, 1H), 7.03–7.00 (m, 2H), 6.98–6.95 (m, 1H), 6.70 (s, 1H), 3.75 (s, 3H), 3.23 (s, 3H) ppm; ^{13}C{1H}(125 MHz, $CDCl_3$) δ 142.9, 141.9, 141.3, 140.9, 140.5, 136.7, 136.3, 131.3, 131.1, 130.4, 129.4, 129.3, 128.5, 127.7, 125.6, 123.2, 122.4, 122.2, 122.0, 120.6, 120.4, 120.2, 120.0, 118.8, 115.1, 111.8, 109.4, 108.8, 33.0, 31.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{34}H_{26}BrN_2$ $[M + H]^+$ 541.1279, found 541.1274.

*4-(9-Methyl-1-(1-methyl-1H-indol-3-yl)-4-phenyl-9H-carbazol-2-yl)benzonitrile (**2n**).* Isolated as a yellowish solid; yield: 79% (0.076 g); mp: 300–301 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.70–7.68 (m, 2H), 7.56–7.53 (m, 2H), 7.51–7.48 (m, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.41–7.39 (m, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.34–7.32 (m, 3H), 7.29–7.26 (m, 2H), 7.25–7.24 (m, 2H), 7.12 (s, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.70 (s, 1H), 3.76 (s, 3H), 3.27 (s, 3H) ppm; ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): 148.0, 142.9, 141.0, 140.7, 139.7, 136.8, 136.2, 131.1, 130.8, 130.3, 129.3, 128.6, 127.8, 125.9, 122.7, 122.4, 122.2, 122.0, 121.1, 120.2, 120.1, 119.3, 119.0, 115.0, 111.3, 109.5, 108.8, 33.0, 31.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{35}H_{26}N_3$ $[M + H]^+$ 488.2127, found 488.2125.

*9-Methyl-1-(1-methyl-1H-indol-3-yl)-2-(naphthalen-2-yl)-4-phenyl-9H-carbazole (**2o**).* Isolated as a yellow solid; yield: 91% (0.088 g); mp: 291–292 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (s, 1H), 7.75 (d, J = 6.5 Hz, 2H), 7.70–7.64 (m, 2H), 7.55 (t, J = 7.0 Hz, 2H), 7.51–7.47 (m, 2H), 7.46–7.43 (m, 2H), 7.41–7.39 (m, 1H), 7.40–7.35 (m, 3H), 7.33 (d, J = 8.0 Hz, 1H), 7.29 (s, 1H), 7.28–7.27 (m, 1H), 7.14–7.09 (m, 2H), 7.00–6.97 (m, 1H), 6.68 (s, 1H), 3.65 (s, 3H), 3.28 (s, 3H) ppm; ^{13}C{1H} NMR ($CDCl_3$, 100 MHz): 143.0, 141.6, 141.5, 141.0, 140.8, 136.6, 136.3, 133.2, 131.9, 131.3, 131.0, 129.6, 129.5, 128.5, 128.4, 128.2, 128.0, 127.6, 127.5, 126.3, 125.6, 125.5, 125.4, 123.9, 122.3, 121.9, 120.5, 119.9, 118.8, 115.4, 112.0, 109.3, 108.8, 32.9, 31.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{38}H_{29}N_2$ $[M + H]^+$ 513.2331, found 513.2330.

*2,9-Dimethyl-1-(1-methyl-1H-indol-3-yl)-4-phenyl-9H-carbazole (**2p**).* Isolated as a white solid; yield: 95% (0.092 g); mp: 88–89 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 2H), 7.49–7.46 (m, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.33–7.28 (m, 3H), 7.21 (d, J = 8.0 Hz, 1H), 7.11–7.10 (m, 1H), 7.08 (s, 1H), 7.06 (m, 1H), 6.94–6.91 (m, 1H), 3.94 (s, 3H), 3.21 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C{1H}(100 MHz, $CDCl_3$) δ 142.3, 141.7, 141.2, 137.0, 136.8, 136.4, 129.7, 129.4, 128.4, 127.4, 125.0, 123.1, 122.5, 122.1, 122.0, 120.5, 119.7, 119.2, 118.5, 115.8, 112.5, 109.4, 108.5, 33.1, 31.4, 20.8 ppm; HRMS (ESI-TOF): m/z calculated for $C_{29}H_{25}N_2$ $[M + H]^+$ 401.2018, found 401.2013.

*9-Methyl-1-(1-methyl-1H-indol-3-yl)-4-phenyl-9H-carbazole (**2q**).* Isolated as a white solid; yield: 95% (0.092 g); mp: 97–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 2 Hz, 1H), 7.54 (d, J = 6.5 Hz, 2H), 7.50–7.48 (m, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.43–7.41 (m, 2H), 7.39 (s, 1H), 7.38–7.36 (m, 1H), 7.31–7.28 (m, 2H), 7.22 (s, 1H), 7.13–7.09 (m, 2H), 6.98–6.95 (m, 1H), 3.93 (s, 3H), 3.45 (s, 3H) ppm; ^{13}C{1H}(125 MHz, $CDCl_3$) δ 142.5, 141.6, 140.2, 136.7, 136.6, 129.9, 129.6, 129.4, 128.5, 127.9, 127.5, 125.5, 122.7, 122.4, 122.1, 121.4, 120.7, 120.5, 119.9, 118.7, 117.2, 114.9, 109.4, 108.8, 33.1, 31.8 ppm; HRMS (ESI-TOF): m/z calculated for $C_{28}H_{23}N_2$ $[M + H]^+$ calculated 387.1861, found 387.1863.

*9-Methyl-1,2,4-triphenyl-9H-carbazole (**2r**).* Isolated as a yellow solid; yield: 80% (0.077 g); mp: 179–180 °C; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 1H), 7.50–7.48 (m, 4H), 7.41 (t, J = 7.0 Hz, 2H), 7.36–7.33 (m, 2H), 7.32–7.30 (m, 5H), 7.28–7.26 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 7.14 (t, J = 8.5 Hz, 1H), 7.11 (s, 1H), 7.04 (t, J = 7.5 Hz, 1H), 3.10 (s, 3H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.0, 140.5, 138.3, 137.2, 136.2, 135.9, 135.7, 133.8, 132.6, 131.8, 131.2, 130.5, 130.3, 129.9, 129.7, 128.5, 128.4, 128.1, 128.0, 127.8, 127.6, 127.2, 126.6, 125.5, 122.2, 121.8, 120.2, 120.1, 110.5, 34.3 ppm; HRMS (ESI-TOF): m/z calculated for $C_{31}H_{24}N$ $[M + H]^+$ 410.1909, found 410.1903.

*9-Benzyl-1,2,4-triphenyl-9H-carbazole (**2s**).* Isolated as a yellow solid; yield: 75% (0.072 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.72 (m, 2H), 7.56–7.53 (m, 2H), 7.51–7.48 (m, 2H), 7.31–7.27 (m, 1H), 7.17 (s, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.12–7.09 (m, 6H), 7.08–7.06 (m, 3H), 7.04–7.02 (m, 2H), 7.00–6.96 (m, 3H), 6.61–6.59 (m, 2H), 5.01 (s, 2H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.6, 142.1, 141.2, 140.8, 139.7, 138.1, 137.5, 136.8, 136.1, 135.9, 135.7, 135.2, 134.4, 134.2, 133.2, 131.9, 131.2, 130.5, 129.9, 129.7, 129.5, 129.1, 128.5, 128.4, 128.1, 128.0, 127.8, 127.3, 127.2, 127.0, 126.9, 126.7, 126.6, 126.3, 126.1, 125.4, 122.7, 122.5, 122.0, 121.8, 121.6, 120.5, 120.4, 120.1, 119.8, 111.8, 110.0, 49.9 ppm; HRMS (ESI-TOF): m/z calculated for $C_{37}H_{28}N$ $[M + H]^+$ 486.2222, found 486.2223.

*9-Allyl-1,2,4-triphenyl-9H-carbazole (**2t**).* Isolated as a yellow solid; yield: 60% (0.057 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (m, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.49–7.46 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H),7.36–7.33 (m, 1H), 7.30–7.28 (m, 2H), 7.27 (s, 1H), 7.25–7.22 (m, 3H), 7.16–7.10 (m, 6H), 6.97 (t, J = 7.0 Hz, 1H), 5.57–5.49 (m, 1H), 4.96 (dd, J_1 = 1.0 Hz, J_2 = 10.5 Hz, 1H), 4.65 (dd, J_1 = 1.0 Hz, J_2 = 16.0 Hz, 1H), 4.32–4.31 (m, 2H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.3, 141.2, 139.9, 138.5, 138.1, 136.6, 133.3, 131.7, 130.3, 129.4, 128.5, 127.6, 127.3, 126.0, 125.6, 123.6, 123.2, 122.4, 119.1, 115.8, 109.7, 46.7 ppm; HRMS (ESI-TOF): m/z calculated for $C_{33}H_{26}N$ $[M + H]^+$ 436.2065, found 436.2063.

*4-Hexyl-9-methyl-1,2-diphenyl-9H-carbazole (**2u**).* Isolated as a yellow solid; yield: 78% (0.075 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 7.5 Hz, 1H), 7.40–7.37 (m, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.21–7.19 (m, 1H), 7.18 (s, 1H), 7.17 (s, 4H), 7.08–7.04 (m, 5H), 7.00 (s, 1H), 3.21 (t, J = 7.5 Hz, 2H), 3.13 (s, 3H), 1.87–1.81 (m, 2H), 1.54–1.47 (m, 2H), 1.34–1.28 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.7, 142.4, 139.7, 139.3, 138.7, 132.1, 130.4, 127.5, 127.4, 126.9, 125.9, 125.2, 122.6, 122.4, 121.9, 120.9, 108.8, 34.6, 32.8, 31.9, 29.8, 29.7, 22.8, 14.2 ppm; HRMS (ESI-TOF): m/z calculated for $C_{31}H_{32}N$ $[M + H]^+$ 418.2535, found 418.2537.

*9-Methyl-4-pentyl-1,2-diphenyl-9H-carbazole (**2v**).* Isolated as a yellow solid; yield: 75% (0.072 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.5 Hz, 1H), 7.48–7.44 (m, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.29–7.27 (m, 1H), 7.26–7.25 (m, 1H), 7.24–7.23 (m, 4H), 7.17–7.10 (m, 5H), 7.07 (s, 1H), 3.28 (t, J = 8.0 Hz, 2H), 3.20 (s, 3H), 1.95–1.89 (m, 2H), 1.61–1.53 (m, 2H), 1.49–1.40 (m, 2H), 0.94 (t, J = 7.5 Hz, 1H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.7, 142.4, 139.7, 139.3, 138.6, 137.1, 132.1, 130.3, 127.5, 127.4, 126.9, 125.9, 125.2, 122.6, 122.5, 122.4, 121.9, 120.9, 119.3, 108.8, 34.5, 32.8, 32.3, 29.5, 22.8, 14.3 ppm; HRMS (ESI-TOF): m/z calculated for $C_{30}H_{30}N$ $[M + H]^+$ 404.2378, found 404.2377.

*9-Methyl-1,2-diphenyl-4-(p-tolyl)-9H-carbazole (**2w**).* Isolated as a yellow solid; yield: 82% (0.079 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.40–7.36 (m, 2H), 7.34–7.33 (m, 2H), 7.32–7.29 (m, 3H), 7.28–7.26 (m, 2H), 7.24 (s, 1H), 7.16–7.15 (m, 2H), 7.14 (s, 2H), 7.13–7.10 (m, 1H), 7.00–6.97 (m, 1H), 3.23 (s, 3H), 2.49 (s, 3H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.9, 142.1, 139.6, 139.3, 138.5, 138.2, 137.3, 136.6, 132.0, 130.4, 129.3, 129.2, 127.6, 127.4, 127.1, 126.0, 125.6, 123.5, 123.0, 122.4, 122.2, 120.5, 118.8, 108.7, 32.8, 21.5 ppm; HRMS (ESI-TOF): m/z calculated for $C_{32}H_{26}N$ $[M + H]^+$ 424.2065, found 424.2066.

*9-Methyl-1,2-diphenyl-4-(4-(trifluoromethyl)phenyl)-9H-carbazole (**2x**).* Isolated as a yellow solid; yield: 83% (0.080 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.71 (m, 4H), 7.36–7.32 (m, 2H), 7.26–7.20 (m, 6H), 7.18 (s, 1H), 7.9–7.08 (m, 4H), 7.06 (d, J = 3.5 Hz, 1H), 7.05 (s, 1H), 6.95–6.92 (m, 1H), 3.18 (s, 3H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.0, 143.0, 141.7, 139.8, 139.4, 138.1, 134.9, 131.9, 130.3, 129.9, 127.7, 127.5, 127.3, 126.2, 126.0, 125.5, 123.9, 123.3, 122.1, 121.7, 120.2, 119.1, 109.0, 32.8 ppm; HRMS (ESI-TOF): m/z calculated for $C_{32}H_{23}F_3N$ $[M + H]^+$ 478.1783, found 478.1783.

*4-([1,1'-Biphenyl]-4-yl)-9-methyl-1,2-diphenyl-9H-carbazole (**2y**).* Isolated as a yellow solid; yield: 80% (0.077 g); mp: 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 3H), 7.76–7.74 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.41–7.37 (m, 3H), 7.33–7.31 (m, 3H), 7.29–7.27 (m, 3H), 7.20 (s, 1H), 7.17–7.16 (m, 2H), 7.15–7.11 (m, 3H), 7.01–6.98 (m, 1H), 3.25 (s, 3H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.9, 142.0, 141.0, 140.4, 140.2, 139.7, 139.4, 138.4, 136.1, 132.0, 130.6, 130.4, 129.9, 129.0, 127.6, 127.4, 127.2, 126.1, 125.7, 126.1, 125.7, 123.5, 123.2, 122.4, 122.1, 120.5, 118.9, 108.4, 32.9 ppm; HRMS (ESI-TOF): m/z calculated for $C_{37}H_{28}N$ $[M + H]^+$ 486.2222, found 486.2221.

*9-Benzyl-1-(1-benzyl-5-methoxy-1H-indol-3-yl)-6-methoxy-2,4-diphenyl-9H-carbazole (**2z**).* Isolated as a yellowish solid; yield: 87% (0.084 g); mp: 185–186 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.0 Hz, 2H), 7.52–7.48 (m, 1H), 7.21 (s, 1H), 7.18–7.12 (m, 6H), 7.11–7.09 (m, 4H), 7.08–7.03 (m, 4H), 7.01–6.99 (m, 1H), 6.98–6.96 (m, 2H), 6.78–6.72 (m, 2H), 6.61 (d, J = 7.0 Hz, 2H), 6.51–6.5 (m, 2H), 6.24 (s, 1H), 5.07 (s, 3H), 4.73–4.60 (m, 1H), 3.69 (s, 3H), 3.61 (s, 3H) ppm; $^{13}C\{1H\}$(125 MHz, $CDCl_3$) δ 154.6, 153.2, 142.8, 142.5, 141.2, 140.8, 139.0, 137.5, 136.6, 131.5, 130.6, 129.7, 129.6, 128.6, 128.4, 128.1, 127.7, 127.3, 127.2, 126.4, 126.2, 125.9, 125.2, 123.1, 122.7, 120.4, 115.3, 114.9, 112.4, 111.0, 110.6, 109.9, 105.3, 101.4, 55.8, 55.6, 49.7, 47.4 ppm; HRMS (ESI-TOF): m/z calculated for $C_{28}H_{23}N_2O_2$ $[M + H]^+$ calculated 675.8520, found 675.8524.

*9-Methyl-2,4-diphenyl-1-(2,4,6-trimethoxyphenyl)-9H-carbazole (**2aa**).* Isolated as a yellow solid; yield: 84% (0.081 g); mp: 186–187 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.0 Hz, 2H), 7.52–7.50 (m, 2H), 7.49–7.43 (m, 2H), 7.36–7.33 (m, 1H),

7.28 (d, J = 8.5 Hz, 1H), 7.19–7.17 (m, 2H), 7.15–7.08(m, 4H), 6.94–6.91 (m, 1H), 6.05 (s, 2H), 3.81 (s, 3H), 3.54 (s, 3H), 3.42 (s, 3H) ppm; $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$): δ 161.5, 159.4, 143.0, 142.4, 141.7, 141.1, 140.1, 136.2, 129.6, 129.2, 128.3, 127.3, 127.0, 125.9, 125.1, 123.2, 122.5, 122.2, 120.2, 118.3, 114.6, 108.7, 108.3, 90.1, 55.6, 55.3, 30.6 ppm; HRMS (ESI-TOF): m/z calculated for $C_{34}H_{30}NO_3$ $[M + H]^+$ 500.2226, found 500.2220.

Conflicts of interest

There are no conflicts to declare.

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References

1 (*a*) R. Hegden, P. B. D. Emmanuel, J. Beevi and S. S. Dharan, *J. Pharm. Sci. Res.*, 2020, **12**, 1271–1277; (*b*) A. Caruso, J. Ceramella, D. Iacopetta, C. Saturnino, M. V. Mauro, R. Bruno, S. Aquaro and M. S. Sinicropi, *Molecules*, 2019, **24**, 1912–1936; (*c*) S. Sellamuthu, G. Gutti, D. Kumar and S. K. Singh, *Mini-Rev. Org. Chem.*, 2018, **15**, 498–507.

2 (*a*) J. Yin, Y. Ma, G. Li, M. Peng and W. Lin, *Coord. Chem. Rev.*, 2020, **412**, 213257–213279; (*b*) I. Gupta and P. E. Kesavan, *Front. Chem.*, 2019, **7**, 841–872; (*c*) K. Karon and M. Lapkowski, *J. Solid State Electrochem.*, 2015, **19**, 2601–2610; (*d*) H. Jiang, J. Sun and J. Zhang, *Curr. Org. Chem.*, 2012, **16**, 2014–2025; (*e*) J. Li and A. C. Grimsdale, *Chem. Soc. Rev.*, 2010, **39**, 2399–2410.

3 (*a*) T. Mandal and J. Dash, *Org. Biomol. Chem.*, 2021, **19**, 9797–9808; (*b*) T. Aggarwal, Sushmita and A. K. Verma, *Org. Biomol. Chem.*, 2019, **17**, 8330–8342; (*c*) S. N. Georgiades and P. G. Nicolau, *Adv. Heterocycl. Chem.*, 2019, **129**, 1–88; (*d*) N. Yoshikai and Y. Wei, *Asian J. Org. Chem.*, 2013, **2**, 466–478; (*e*) A. W. Schmidt, K. R. Reddy and H.-J. Knölker, *Chem. Rev.*, 2012, **112**, 3193–3328; (*f*) X. Fang, L. Fang and S. Gou, *Chin. J. Org. Chem.*, 2012, **32**, 1217–1231; (*g*) H.-J. Knölker and K. R. Reddy, *Chem. Rev.*, 2002, **102**, 4303–4428.

4 (*a*) J. Zhou, Y. Qiu, J. Li, C. Fu, X. Zhang and S. Ma, *Chem. Commun.*, 2017, **53**, 4722–4725; (*b*) W. Kong, C. Fu and S. Ma, *Org. Biomol. Chem.*, 2012, **10**, 2164–2173; (*c*) W. Kong, C. Fu and S. Ma, *Chem. Commun.*, 2009, 4572–4574.

5 (*a*) B. Alcaide, P. Almendros, J. M. Alonso, E. Busto, I. Fernández, M. P. Ruiz and G. Xiaokaiti, *ACS Catal.*, 2015, **5**, 3417–3421; (*b*) Y. Qiu, J. Zhou, C. Fu and S. Ma, *Chem. – Eur. J.*, 2014, **20**, 14589–14593; (*c*) Y. Qiu, W. Kong, C. Fu and S. Ma, *Org. Lett.*, 2012, **14**, 6198–6201; (*d*) L. Wang, G. Li and Y. Liu, *Org. Lett.*, 2011, **13**, 3786–3789; (*e*) C. Praveen and P. T. Perumal, *Synlett*, 2011, 521–524.

6 (*a*) N. Inprung, M. J. James, R. J. Taylor and W. P. Unsworth, *Org. Lett.*, 2021, **23**, 2063–2068; (*b*) A. K. Clarke, H. E. Ho, J. A. Rossi-Ashton, R. J. Taylor and W. P. Unsworth, *Chem. – Asian J.*, 2019, **11**, 1900–1911.

7 A. Banerjee, S. Kundu, A. Bhattacharyya, S. Sahu and M. S. Maji, *Org. Chem. Front.*, 2021, **8**, 2710–2771.

8 For examples of *exo*-cyclizations, see: (*a*) J. Zhu, J. Li, L. Zhang, S. Sun, Z. Wang, X. Li, L. Yang, M. Cheng, B. Lin and Y. Liu, *J. Org. Chem.*, 2023, **88**, 5483–5496; (*b*) S. Yaragorla, R. Dada and D. Bag, *Eur. J. Org. Chem.*, 2019, 6983–6988; (*c*) S. Yaragorla, D. Bag, R. Dada and K. J. Jose, *ACS Omega*, 2018, **3**, 15024–15034; (*d*) R. Sanz, D. Miguel, M. Mohain, P. García-García, M. A. Fernández-Rodríguez, A. González-Pérez, O. Nieto-Faza, A. R. de Lera and F. Rodríguez, *Chem. – Eur. J.*, 2010, **16**, 9818–9828; (*e*) R. Sanz, D. Miguel and F. Rodríguez, *Angew. Chem., Int. Ed.*, 2008, **47**, 7354–7357; (*f*) C. Ferrer, C. H. M. Amijs and A. M. Echavarren, *Chem. – Eur. J.*, 2007, **13**, 1358–1373.

9 (*a*) S. J. Heffernan, J. P. Tellam, M. E. Queru, A. C. Silvanus, D. Benito, M. F. Mahon, A. J. Hennessy, B. I. Andrews and D. R. Carbery, *Adv. Synth. Catal.*, 2013, **355**, 1149–1159; (*b*) C. J. Loh, J. Badorrek, G. Raabe and D. Enders, *Chem. – Eur. J.*, 2011, **17**, 13409–13414; (*c*) X. Xie, X. Du, Y. Chen and Y. Liu, *J. Org. Chem.*, 2011, **76**, 9175–9181; (*d*) Y. Lu, X. Du, X. Jia and Y. Liu, *Adv. Synth. Catal.*, 2009, **351**, 1517–1522.

10 (*a*) A. S. K. Hashmi, W. Yang and F. Rominger, *Chem. – Eur. J.*, 2012, **18**, 6576–6580; (*b*) G. Li and Y. Liu, *J. Org. Chem.*, 2010, **75**, 3526–3528.

11 Z. Zhang, X. Tang, Q. Xu and M. Shi, *Chem. – Eur. J.*, 2013, **19**, 10625–10631.

12 M. J. James, R. E. Clubley, K. Y. Palate, T. J. Procter, A. C. Wyton, P. ÓBrien, R. J. K. Taylor and W. P. Unsworth, *Org. Lett.*, 2015, **17**, 4372–4375.

13 (*a*) A. Suárez, S. Suárez-Pantiga, O. Nieto-Faza and R. Sanz, *Org. Lett.*, 2017, **19**, 5074–5077; (*b*) M. Solas, M. A. Muñoz-Torres, F. Martínez-Lara, L. Renedo, S. Suárez-Pantiga and R. Sanz, *ChemPlusChem*, 2023, **88**, e2023003, DOI: **10.1002/cplu.202300382**.

14 P. Tharra and B. Baire, *Org. Lett.*, 2018, **20**, 1118–1121.

15 (*a*) L. Ali, D. S. Latha, A. Kumar and S. Yaragorla, *J. Org. Chem.*, 2023, **88**, 5457–5472; (*b*) S. Yaragorla and D. Arun, *J. Org. Chem.*, 2022, **87**, 14250–14263; (*c*) S. Yaragorla and D. S. Latha, *ACS Omega*, 2022, **7**, 34693–34706; (*d*) J. Vannada, M. Sulthan, D. Arun, R. Dada and S. Yaragorla, *J. Org. Chem.*, 2020, **85**, 6697–6708; (*e*) R. Dada, M. Sulthan and S. Yaragorla, *Org. Lett.*, 2020, **22**, 279–283; (*f*) S. Yaragorla and A. Pareek, *Eur. J. Org. Chem.*, 2018, 1863–1871.

16 (*a*) H. F. Motiwala, A. M. Armaly, J. G. Cacioppo, T. C. Coombs, K. R. K. Koehn, V. M. Norwood IV and J. Aubé, *Chem. Rev.*, 2022, **122**, 12544–12747; (*b*) V. Pozhydaiev, M. Power, V. Gandon, J. Moran and D. Lebœuf, *Chem. Commun.*, 2020, **56**, 11548–11564, and references cited therein.