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Regioselective Synthesis of Elusive 4,9-Dihydro-1*H*-Carbazoles by Gold-Catalyzed Cycloisomerization of 3-Allenylmethylindoles

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Supporting Information

ABSTRACT: A general and efficient synthesis of 4,9-dihydro-1*H*-carbazoles from 3-allenylmethylindoles is reported. The process, catalyzed by a cationic gold(I) complex, involves a formal C2−H bond activation of the indole unit by reaction with the allene. The nature of the substituents at the allylic and terminal positions of the allene moiety has a crucial effect on the regioselectivity of the cyclization, which is also influenced by the catalyst and the solvent employed. Moreover, some evidence of the contribution of different reaction routes is provided, which led us to propose a plausible multipathway mechanism consistent with all of the results described.

INTRODUCTION

The carbazole unit is a key heterocyclic structure that is present in a broad range of natural products possessing biological activity[1,2] and in molecules having interesting applications in materials science.[3−5] Therefore, numerous approaches for their preparation have been described.[1] However, the synthesis of the related tetrahydro-[6−9] and dihydrocarbazoles[10−13] has received less attention. For instance, no efficient methodologies to access 4,9-dihydro-1*H*-carbazoles have been developed, even though this heterocyclic skeleton is found in diverse natural products such as dihydrotubingensins A and B (Figure 1).[14] The scarce

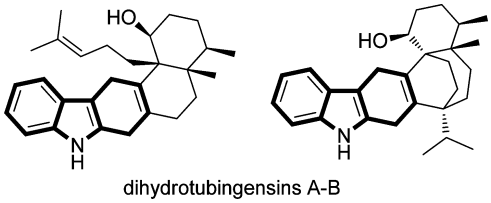
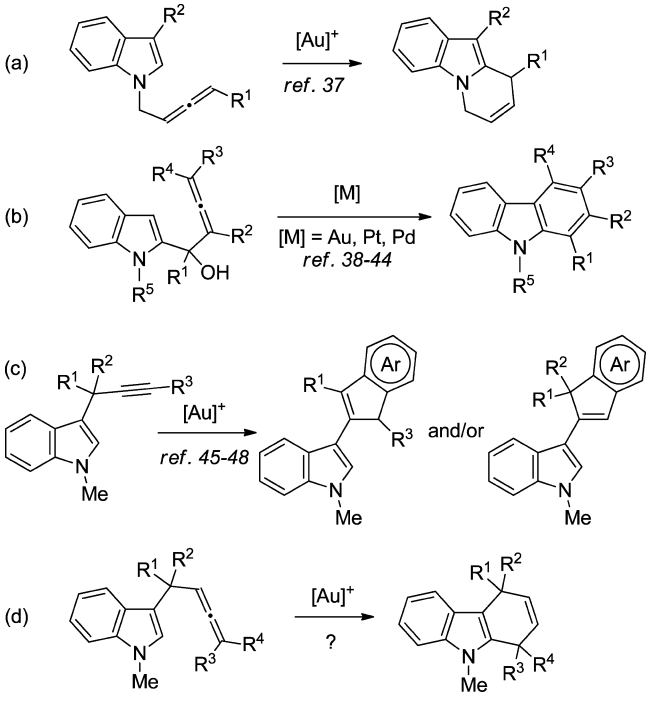


Figure 1. Naturally occurring 4,9-dihydro-1*H*-carbazoles.

reported syntheses of such dihydrocarbazoles are limited to particular examples of [4 + 2] intra-[15] or intermolecular[16−18] cycloadditions of in situ-generated indole-2,3-quinodimethanes with acetylenes or ring-closing methathesis.[19]

On the other hand, transition-metal-catalyzed cycloisomerization of enynes[20] and functionalized allenes[21,22] has become a powerful strategy for the synthesis of cyclic compounds. In this regard, gold-catalyzed reactions of alkyne-functionalized indoles allow the construction of a wide range of heteropolycyclic frameworks.[23−33] However, related cycloisomerizations of indoles with a tethered allene have been less studied.[34−36] In particular, a gold-catalyzed hydroarylation of *N*-allenylmethylindoles that furnishes dihydropyrido[1,2-*a*]-1*H*-indoles has been described (Scheme 1a).[37] Moreover, several cyclizations

Scheme 1. Reported Cycloisomerizations of Allenylmethyl- and Propargylindoles and Proposed Synthesis of Dihydrocarbazoles



of 1-(indol-2-yl)allenols (functionalized 2-allenylmethylindoles) that afford carbazoles have been developed using different metals such as Au,[38−40] Pt,[41−43] and Pd[44] (Scheme 1b).

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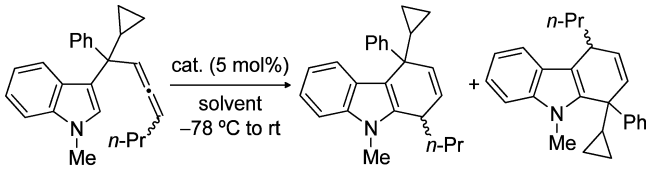
In this context, and taking advantage of our experience in the gold-catalyzed isomerization of 3-propargylindoles to produce 2-(indol-3-yl)indenes (Scheme 1c),[45−48] we envisioned that unexplored 3-allenylmethylindoles could be suitable substrates for the development of a general and efficient synthesis of 4,9-dihydro-1*H*-carbazoles (Scheme 1d).

RESULTS AND DISCUSSION

Toward our aim, we initially selected the disubstituted allene derivative 3-(1-cyclopropyl-1-phenylhepta-2,3-dien-1-yl)-1-methyl-1*H*-indole (**1a**) as model substrate. Preliminary essays conducted at rt in the presence of $Ph_3PAuNTf_2$ as the catalyst afforded a complex mixture of compounds. Pleasantly, a clean cycloisomerization selectively occurred by setting up the reaction at −78 °C and allowing the mixture to reach rt, which afforded a 1/2.3 mixture of regioisomers **2a** and **3a** (Table 1, entry 1). On

Table 1. Cycloisomerization of 3-Allenylmethylindole 1a: Effect of the Reaction Conditions on the Selectivity



1a **2a** **3a**

entry	catalyst	solvent	2a/3a[a]
1	$Ph_3PAuNTf_2$	CH_2Cl_2	1/2.3
2	Ph_3PAuCl	CH_2Cl_2	–
3	$AgNTf_2$	CH_2Cl_2	–
4	$XPhosAuNTf_2$	CH_2Cl_2	1/1.2[b]
5	$Ph_3PAuCl/AgNTf_2$	CH_2Cl_2	2/1
6	$Ph_3PAuNTf_2/AgCl$	CH_2Cl_2	1.2/1
7	$IPrAuCl^c/AgNTf_2$	CH_2Cl_2	2.2/1[b]
8	$(PhO)_3PAuCl/AgNTf_2$	CH_2Cl_2	2.6/1
9	$(2,4\text{-}(t\text{Bu})_2C_6H_3O)_3PAuCl/AgNTf_2$	CH_2Cl_2	2.1/1
10	$Ph_3PAuCl/AgOTf$	CH_2Cl_2	2.8/1
11	$Ph_3PAuCl/AgBF_4$	CH_2Cl_2	2.5/1
12	$Ph_3PAuCl/AgOTs$	CH_2Cl_2	2.5/1
13	$Ph_3PAuCl/AgSbF_6$	CH_2Cl_2	2.3/1
14	$Ph_3PAuNTf_2$	DCE	1/1.9
15	$Ph_3PAuNTf_2$	$C_6H_5CF_3$	1/1.4
16	$Ph_3PAuNTf_2$	DME	4.3/1
17	$Ph_3PAuNTf_2$	THF	4.3/1
18	$Ph_3PAuNTf_2$	MeOH	4.3/1
19	$Ph_3PAuNTf_2$	toluene	4.6/1
20	$(PhO)_3PAuCl/AgNTf_2$	toluene	6.9/1
21	$(PhO)_3PAuCl/AgOTf$	toluene	>10/1

[a]Determined by ^1H NMR analysis of the crude mixture after complete conversion (4−6 h). [b]Several unidentified compounds were also formed. [c]IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

the contrary, no evolution of the allene derivative was observed in reactions in the presence of other metal salts or Lewis acids such as $PtCl_2$, $GaCl_3$, or $Sc(OTf)_3$. Interestingly, the formation of **3a** implies a formal alkyl migration by breaking one and creating two new C−C bonds. The influence of the catalyst and reaction conditions in the process was then investigated. The same ratio of regioisomers (1/2.3) was obtained in reactions conducted at −50 °C or at other temperatures between rt and −78 °C. No reaction was observed with either Ph_3PAuCl or $AgNTf_2$ (entries 2 and 3), whereas a messy reaction and a decrease in the selectivity was observed with $XPhosAuNTf_2$ (entry 4). Remarkably, a switch in the regioselectivity occurred when an equimolecular mixture of PPh_3AuCl and $AgNTf_2$ was used as the catalyst (entry 5). Analogous experiments using catalysts derived from NHC or phosphite ligands also produced cycloadduct **2a** as the major isomer in comparable ratios (entries 7−9). The switch in the regioselectivity (entry 1 vs 5) could be associated with a noninnocent presence of the silver salt.[49] This assumption was confirmed by an experiment conducted with the combination of PPh_3AuNTf_2 and AgCl as the catalyst, which also switched the regioselectivity to give in this case a **2a**/**3a** ratio of 1.2/1 (entry 6). These results support the complexity of the gold/silver catalysis mechanisms pointed out by Shi.[49]

On the other hand, although a minor influence of the catalyst counterion in the outcome of the process was determined, the **2a**/**3a** product ratio could be slightly improved using a triflate anion (entry 10 vs entries 11−13). In contrast, the solvent has a crucial effect on the regioselectivity. Thus, reactions catalyzed by $Ph_3PAuNTf_2$ and conducted in CH_2Cl_2, DCE, or trifluorotoluene gave **3a** as the major isomer, while analogous experiments conducted in a nonhalogenated solvent such as DME, THF, MeOH, or toluene switched the selectivity to **2a** (entries 1, 14, and 15 vs 16−19). A similar trend was found in reactions catalyzed by $(PhO)_3PAuCl/AgNTf_2$ (entry 8 vs 20). Furthermore, by using this phosphite-derived gold complex and changing the catalyst counterion to triflate, which we had previously observed to favor the formation of **2a**, we were able to obtain dihydrocarbazole **2a** nearly exclusively (entry 21).

Notably, our studies of the reaction conditions showed that an appropriate selection of catalyst and solvent allows the selective formation of both dihydrocarbazole isomers **2a** and **3a** from allenylmethylindole **1a**: the combination $(PhO)_3PAuCl/AgOTf$/toluene (method A) selectively produces **2a**, whereas PPh_3AuNTf_2/CH_2Cl_2 (method B) predominantly furnishes **3a**.

Once method A and method B were established as the best conditions for selectively obtaining dihydrocarbazoles **2a** and **3a**, respectively, we decided to explore the influence of the starting substrate on the process outcome and the scope of both cycloisomerizations. Initially, we prepared various allenylmethylindoles **1** possessing a quaternary allylic carbon and a di- or trisubstituted allene moiety (R^1, R^2, $R^3 \neq H$) from 3-propargylindoles **4** and **5**. These derivatives were easily accessible from simple and commercially available *N*-methylindole, carbonyl, and alkyne compounds by application of our previously developed Brønsted acid-catalyzed direct substitution of propargylic alcohols (Scheme 2a).[45,50,51] Then, using Myers conditions,[52] i.e., the addition of alkynol **4** to a mixture of PPh_3 and diisopropyl azodicarboxylate (DIAD) followed by the addition of *o*-nitrobenzenesulfonylhydrazide (NBSH),[53] allene derivatives **1a−i** were obtained in good yields (Scheme 2b). On the other hand, benzyl-functionalized acetylenes **5** were efficiently transformed in the corresponding allenes **1j−m** by base-promoted isomerization using KOH[54] or *t*-BuLi (Scheme 2c).

Having synthesized allenylmethylindoles **1a−m** bearing different substituents (R^1−R^4), we investigated their reactions using method A (Table 2) and method B (Table 3). As previously observed for **1a** (Table 2, entry 1), under method A the reactions of disubstituted allenes **1b−k** (R^4 = H) (Table 2, entries 2−11) as well as trisubstituted allene derivatives **1l** and **1m** ($R^4 \neq H$, entries 12 and 13) bearing aryl, linear alkyl, or branched alkyl groups at both the allylic and terminal allene positions essentially or exclusively afforded regioisomer **2**.

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Scheme 2. Synthesis of Allenylmethylindoles 1a−i and 1j−m

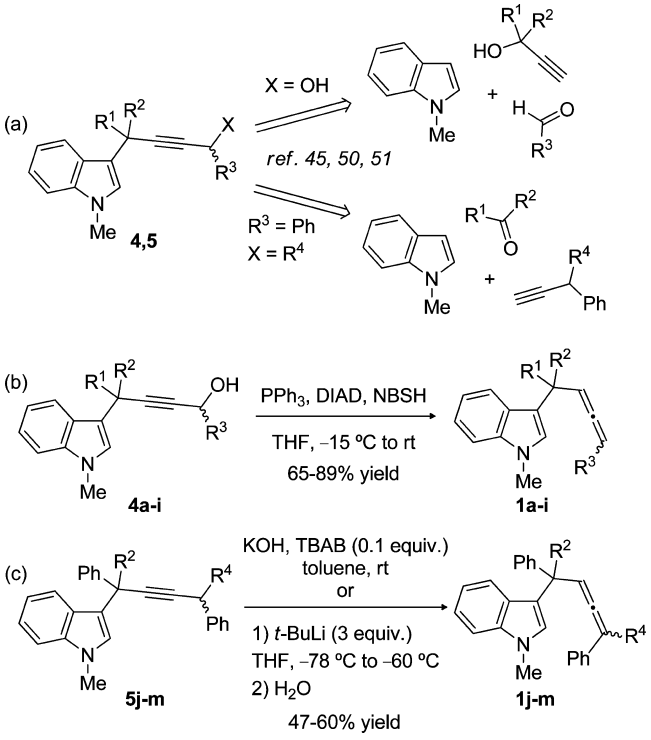
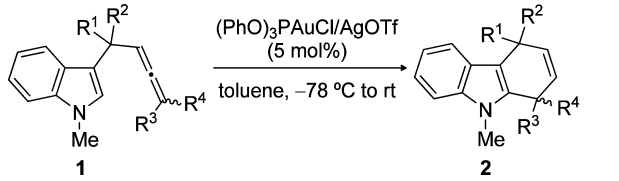


Table 2. Cycloisomerization of 3-Allenylmethylindoles 1a−m Using Method A: Regioselective Synthesis of 4,9-Dihydro-1*H*-carbazoles 2[a]



entry	1	R^1	R^2	R^3	R^4	2	yield (%)[b]
1	**1a**	Ph	*c*-Pr	*n*-Pr	H	**2a**	78
2	**1b**	Ph	Ph	*n*-Pr	H	**2b**	91
3	**1c**	*c*-Pr	*c*-Pr	*n*-Pr	H	**2c**	57
4	**1d**	Me	*c*-Pr	*n*-Pr	H	**2d**	64
5	**1e**	Me	Me	*n*-Pr	H	**2e**	80
6	**1f**	Ph	*c*-Pr	Me	H	**2f**	57[c]
7	**1g**	4-ClC_6H_4	*c*-Pr	Me	H	**2g**	66[c]
8	**1h**	Ph	*i*-Pr	Me	H	**2h**	76[c]
9	**1i**	Ph	*c*-Pr	*i*-Pr	H	**2i**	70[c]
10	**1j**	Ph	*c*-Pr	Ph	H	**2j**	80
11	**1k**	Ph	Ph	Ph	H	**2k**	78
12	**1l**	Ph	*c*-Pr	Ph	Me	**2l**	86
13	**1m**	Ph	*c*-Pr	Ph	Ph	**2m**	25[d]

[a]Reactions required 4−6 h to reach completion and products **2** were exclusively formed (regioselectivity >20/1), unless otherwise stated. [b]Isolated yields. [c]**2**/**3** ratios: 3.6/1 (entry 6), 3.8/1 (entry 7), 6.7/1 (entry 8), 5.0/1 (entry 9). [d]41% conversion.

Therefore, the use of method A afforded a series of highly substituted 4,9-dihydro-1*H*-carbazoles **2a−m** regioselectively in good yields. In all of the reactions displayed in Table 2 as well as in the ones described later in this paper (depicted in Table 3 and Schemes 4 and 5), the major regioisomer was obtained as a ∼1/1 mixture of diastereomers and could be easily isolated from the minor regioisomer.[55] Furthermore, the structures of the final products were established by NMR experiments.

In contrast, parallel experiments conducted using method B revealed a significant influence of the substitution pattern of the substrate on the selectivity of the cycloisomerization. Thus, whereas the formation of dihydrocarbazole **3a** from the model substrate **1a** was favored (Table 3, entry 1), reactions of related derivatives **1b−e** (R^3 = *n*-Pr) mainly afforded dihydrocarbazoles **2b−e** with variable quantities of **3b−e** depending on the substitution at the allylic carbon (Table 3, entries 2−5). In this sense, the presence of an aromatic group at this position seems to be necessary to obtain regioisomer **3** in appreciable amounts. Moreover, the steric hindrance of the R^3 substituent has a crucial effect on the product distribution, as we determined by analyzing the reactions of substrates **1f**, **1a**, and **1i** (R^3 = Me, *n*-Pr, and *i*-Pr, respectively). We can conclude that with method B, the selectivity of the isomerization to dihydrocarbazole **3** can be notably improved by increasing the bulkiness of the alkyl group located at the terminal sp^2 allene carbon atom (Table 3, entry 6 vs 1 vs 9). On the contrary, isomers **2** appear to be totally favored for substrates **1j** and **1k** bearing R^3 = Ph (Table 3, entries 10 and 11). In addition, reactions of trisubstituted allene derivatives **1l** and **1m** (R^3, $R^4 \neq$ H) led mostly to decomposition under these conditions (Table 3, entries 12 and 13). Therefore, among the highly substituted allene derivatives **1a−m** investigated using method B, only **1a** and **1i** afforded useful synthetic yields of the corresponding 4,9-dihydro-1*H*-carbazoles **3a** and **3i** (Table 3, entries 1 and 9), whereas dihydrocarbazoles **3b**, **3f**, and **3g** were obtained in modest yields (Table 3, entries 2, 6, and 7).

Next, we turned our attention to the isomerization of substrates **1n−r** possessing a terminal allene, which were also easily prepared using Myers methodology.[52] Preliminary experiments conducted with allenylmethylindole **1n** gave dihydrocarbazole **3n** as the major regioisomer with a moderate **3**/**2** ratio regardless of the method used (Scheme 3). Further attemps to optimize the reaction conditions in order to increase the regioselectivity for **3n** or to favor the formation of **2n** were unsuccessful.

Nevertheless, with method B, dihydrocarbazole **3n** could be isolated in a reasonable 60% yield (Scheme 4). In the same way, 4,9-dihydro-1*H*-carbazoles **3o−r** were obtained in a regioselective fashion, although usually with a modest ratio, and isolated in moderate to good yields from the corresponding starting allenes **1o−r** (Scheme 4).[55]

To complete the study of the influence of the substitution on the process outcome, allenylmethylindoles **1s−v** with a tertiary or secondary allylic carbon instead a quaternary one were prepared. Notably, the reactions of all of these substrates cleanly and exclusively produced 4,9-dihydro-1*H*-carbazoles **2s−v** in good yields regardless of the reaction conditions employed and the substitution of the starting substrate **1** (Scheme 5). Unexpectedly, these dihydrocarbazoles were completely stable, and no spontaneous dehydrogenation reaction to give the corresponding carbazoles was observed under the reaction conditions or during the purification. Moreover, it is worth mentioning that even for allenylmethylindoles **1t** and **1u** having a terminal allene moiety, the formation of the corresponding 4,9-dihydro-1*H*-carbazoles **3t** and **3u** was totally suppressed using either method A or method B. These results are in sharp contrast to reactions of substrates **1n−r** possessing a terminal allene moiety and a quaternary allylic carbon, which afforded **3** as the major regioisomer regardless of the method used (Scheme 4). On the other hand, the structure of the final products **2s−v** was

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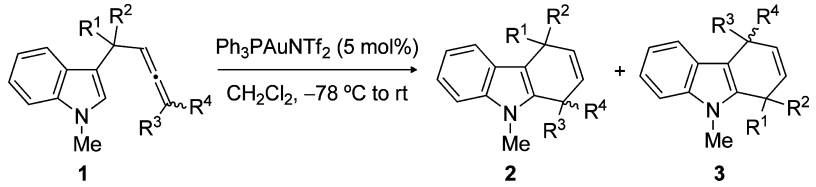
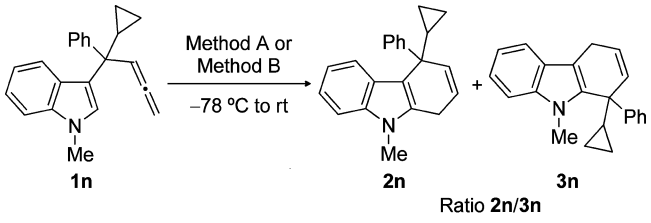
Table 3. Effect of the Structure of the Substrate on the Selectivity of the Cycloisomerization of 3-Allenylmethylindoles 1a−m Using Method B



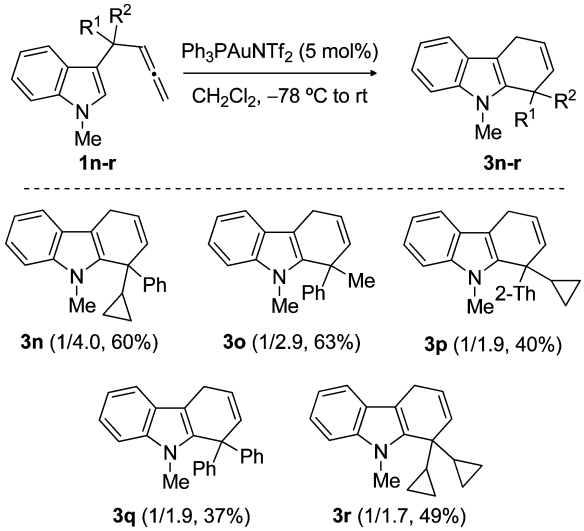
entry	1	R^1	R^2	R^3	R^4	2/3[a]	3	yield (%)[b]
1	**1a**	Ph	*c*-Pr	*n*-Pr	H	1/2.3	**3a**	65
2	**1b**	Ph	Ph	*n*-Pr	H	2.1/1	**3b**	20
3	**1c**	*c*-Pr	*c*-Pr	*n*-Pr	H	7.0/1	**3c**	–
4	**1d**	Me	*c*-Pr	*n*-Pr	H	>10/1	**3d**	–
5	**1e**	Me	Me	*n*-Pr	H	>20/1	**3e**	–
6	**1f**	Ph	*c*-Pr	Me	H	1.3/1	**3f**	24
7	**1g**	4-ClC_6H_4	*c*-Pr	Me	H	1.5/1	**3g**	28
8	**1h**	Ph	*i*-Pr	Me	H	4.4/1	**3h**	–
9	**1i**	Ph	*c*-Pr	*i*-Pr	H	1/>10	**3i**	72
10	**1j**	Ph	*c*-Pr	Ph	H	>20/1	**3j**	–
11	**1k**	Ph	Ph	Ph	H	>20/1	**3k**	–
12	**1l**	Ph	*c*-Pr	Ph	Me	–[c]	**3l**	–
13	**1m**	Ph	*c*-Pr	Ph	Ph	–[c]	**3m**	–

[a]Determined by ^{1}H NMR analysis of the crude product mixtures. Reactions required 4−6 h, and only products **2** and/or **3** were formed, unless otherwise stated. [b]Isolated yields. [c]Decomposition was observed.

Scheme 3. Cycloisomerization of Allenylmethylindole 1n



Scheme 4. Synthesis of 4,9-Dihydro-1*H*-carbazoles 3n−r from Allenylmethylindoles 1n−r Bearing a Terminal Allene Moiety[a]



[a]All of the products were obtained using method B with the exception of substrate **3p**, which was prepared using method A. The **2**/**3** regioisomer ratios and the isolated yields of dihydrocarbazoles **3** are given in parentheses.

again established by NMR experiments and confirmed by X-ray diffraction analysis of **2u**.[56]

This comprehensive study revealed that 3-allenylmethylindoles **1** bearing a di- or trisubstituted allene moiety regioselectively react to produce 4,9-dihydro-1*H*-carbazoles **2** in good yields and, on the other hand, that the formation of compounds **3** from allenylmethylindoles **1** bearing a quaternary center at the allylic carbon is favored using method B provided that the terminal carbon of the allene is unsubstituted or just monosubstituted with a bulky alkyl group. The newly synthesized heterocycles **2** could be mono-, di-, tri-, and tetrasubstituted at the sp^3 carbons of the tricyclic core, and moreover, the substitution can include aryl, linear alkyl, or branched alkyl groups at both positions. In addition, regioisomeric 4,9-dihydro-1*H*-carbazoles **3a**, **3i**, and **3n−r** were synthesized in moderate to good yields from the corresponding starting substrates **1a**, **1i**, and **1n−r** in a regioselective fashion using method B.

A mechanism that would explain the formation of products **2** and **3** is illustrated in Scheme 6. The reaction would be initiated by coordination of the catalyst to the allene followed by intramolecular attack of the indole that may occur at either activated carbon of intermediate **6** to furnish spirocycle species **7** (path a) or **8** (path b).[57] The cyclopropane-containing intermediate **7** would evolve by a 5-*exo* cyclization to give gold carbenoid **9**, whose rearomatization would trigger a cyclopropane ring opening/protodemetalation sequence to yield dihydrocarbazole **2** through vinylgold intermediate **10**. On the other hand, at least three different evolutions of intermediate **8** could be possible. One of them, involving alkyl migration of the carbon supporting R^3 and R^4 (path b_1), would also account for the formation of isomer **2** via intermediates **11** and **10**. However, the alternative 1,2-alkyl shift (path b_2) and subsequent protodemetalation of cationic gold intermediate species **12**

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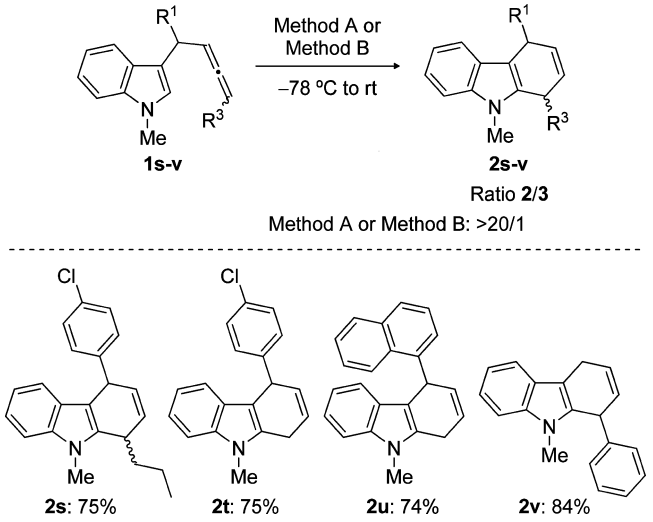
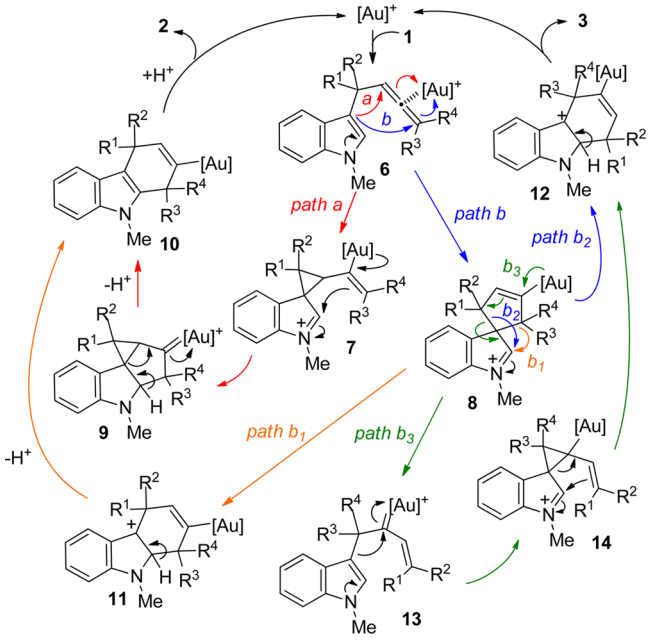
Scheme 5. Synthesis of 4,9-Dihydro-1*H*-carbazoles 2s−v from Allenylmethylindoles 1s−v Possessing a Tertiary or Secondary Allylic Carbon[a]



[a]The products were obtained using method A [$(PhO)_3PAuCl/AgOTf$ (5 mol %), toluene] with the exception of substrate **2u**, which was prepared using method B [$Ph_3PAuNTf_2$ (5 mol %), CH_2Cl_2].

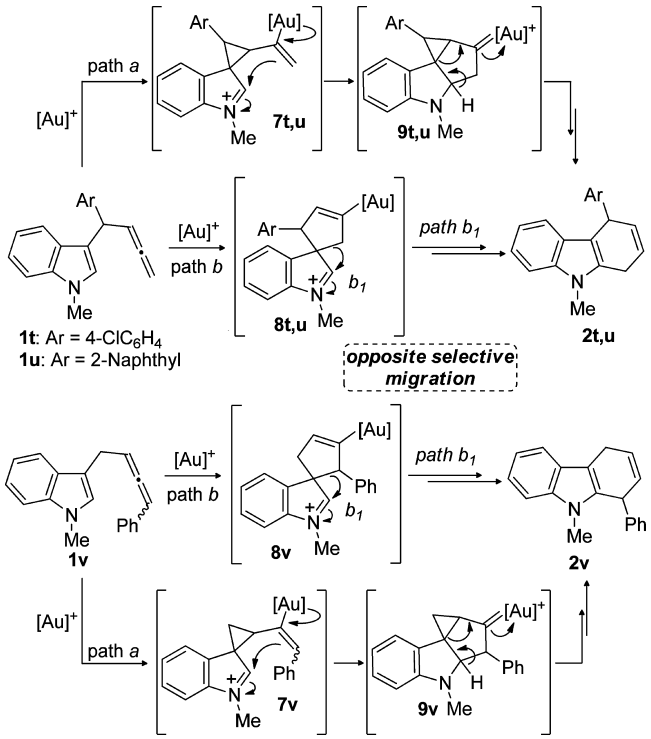
Scheme 6. Proposed Mechanism



would render regioisomer **3**. Moreover, a related stepwise pathway b_3 assisted by the metal that involves the formation of gold carbenoid species **13** would be also plausible. This intermediate would undergo indole nucleophilic addition to the gold carbenoid, giving rise to new spirocyclic derivative **14**, which by a cyclization/ring opening/protodemetalation sequence would afford dihydrocarbazole **3**. Taking into account the data exposed above, we consider at this point that most probably, and depending on the catalyst and the substrate used, all of the proposed pathways could be operative.

In fact, we have obtained some evidence for the viability of paths a and b_3. As illustrated in Scheme 5, the reactions of **1t−v** selectively afford products **2t−v**, which on the basis of our proposal should be formed through pathway a and/or b_1 (Schemes 6 and 7). As shown in Scheme 7, if path b_1 were the

Scheme 7. Evidence for the Viability of Pathway a: Cycloisomerization of Allenylmethylindoles 1t−v



only operative route, this would imply an opposite selective migration of the benzylic versus primary alkyl group in the corresponding intermediates **8** (compare intermediates **8t** and **8u** with **8v**). Therefore, path a must be the running mechanism for at least one of these types of substrates. Furthermore, the effect of steric bulk at R^3 using method B conditions, i.e., the improved selectivity for compound **3** with increasing steric hindrance at R^3 (Me vs *n*-Pr vs *i*-Pr; Table 3, entries 6, 9, and 1, respectively), also accounts for the viability of path a. With a bulkier substituent at R^3, it seems that intermediate **8** would prefer to evolve through path b_1 to release steric hindrance at the transition state. That would lead to **2**, which is not consistent with our observations. Therefore, path a would be more likely to explain these results, which would be logical considering that the formation of **7** from **6** should be favored over the formation of **8** with increased steric bulk at R^3.

On the other hand, pathway b_3 is partially at work in the case of **1q**, as pointed out by the minor formation of indene **15**, which could take place via an iso-Nazarov cyclization of the corresponding intermediate **13q** (Scheme 8). This cyclization could also be considered as a Friedel−Crafts-type reaction.

CONCLUSION

We have described a gold(I)-catalyzed cyclization of 3-allenylmethylindole derivatives that provides access to elusive 4,9-dihydro-1*H*-carbazoles. The process, whose regioselectivity seems to be influenced by both the substrate and the reaction conditions (catalyst and solvent), involves a formal C2−H bond functionalization of the indole unit with the allene. The synthetic utility of this transformation is illustrated by the preparation of several new dihydrocarbazoles with a wide variety of substitution

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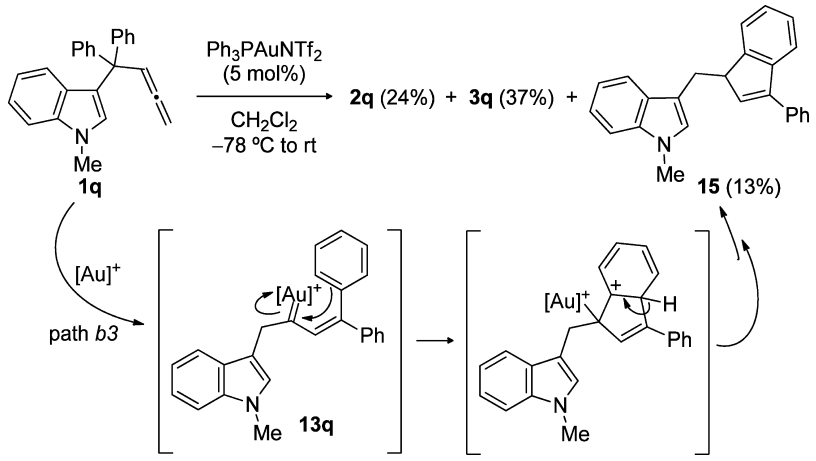
Scheme 8. Evidence for the Viability of Pathway b_3: Formation of Indene 15 in the Reaction of Allenylmethylindole 1q



patterns in usually good yields. Moreover, a plausible mechanism that involves multiple pathways has been proposed, and some insight into the viability of two of these possible routes has been obtained.

EXPERIMENTAL SECTION

General. All reactions involving air-sensitive compounds were carried out under a nitrogen atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated, and purged with N_2. All common reagents, catalysts, and solvents were obtained from commercial suppliers and used without any further purification. Solvents were dried by standard methods. Hexane and ethyl acetate were purchased as extra-pure-grade reagents and used as received. Gold and silver catalysts were purchased from Aldrich or Strem. TLC was performed on aluminum-backed plates coated with silica gel 60 containing F_{254} indicator; the chromatograms were visualized under UV light and/or by staining with a Ce/Mo reagent and subsequent heating. R_f values on silica gel are reported. Flash column chromatography was carried out on silica gel 60 (230−240 mesh). Deactivated silica gel was obtained by stirring with an aqueous K_2HPO_4 solution for 3 h and subsequent filtration and drying at 140 °C for 3 days. NMR spectra were measured on 300 and 400 MHz spectrometers. For ^{1}H NMR spectra, the splitting pattern abbreviations are s, singlet; bs, broad singlet; d, doublet; t, triplet; at, apparent triplet; aq, apparent quartet; sept, septet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; ddd, doublet of doublets of doublets; ddt, doublet of doublets of triplets; dtd, doublet of triplets of doublets; tdd, triplet of doublets of doublets; and m, multiplet. The chemical shifts are reported in parts per million using the residual solvent peak as a reference. ^{13}C NMR spectra were recorded at 75.4 or 100.6 MHz using broadband proton decoupling, and the chemical shifts are reported in parts per million using residual solvent peaks as references. The multiplicities were determined by DEPT experiments. High-resolution mass spectrometry (HRMS) was performed using EI at 70 eV on an instrument equipped with an ion-trap analyzer. Melting points were measured using open capillary tubes and are uncorrected. GC−MS and low-resolution mass spectrometry (LRMS) measurements were recorded on an instrument equipped with an HP-5MS column.

Synthesis of Allenylmethylindoles 1. The starting allenylmethylindoles **1a−i** and **1n−v** were prepared using Myers methodology,[52] whereas **1j** and **1k** were obtained from the corresponding alkyne derivatives by isomerization with KOH.[54] Allenylmethylindoles **1l** and **1m** were synthesized using the following base-promoted procedure: To a solution of the appropriate alkyne **5** (2 mmol) in THF (2 mL) at −78 °C was added dropwise *t*-BuLi (3 equiv, 6 mmol, 3.5 mL of a 1.7 M solution in pentane). After the mixture was stirred for 1 h, the temperature was allowed to increase to −65 °C (for 1 h). At this temperature, the reaction was quenched by the addition of 2 mL of THF/water (1/1), and the mixture was allowed to reach room temperature and then extracted with Et_2O. The organic phase was dried over anhydrous $NaSO_4$, and the solvent was removed under vacuum. The resulting crude residue was purified by column chromatography using hexane/Et_2O (40/1) as the eluent to obtain the corresponding allenylmethylindoles **1l** and **1m** in the yields reported below.

Characterization and Spectroscopic Data for Allenylmethylindoles 1. *3-(1-Cyclopropyl-1-phenylhepta-2,3-dien-1-yl)-1-methyl-1H-indole (**1a**).* Colorless oil; yield = 80% (273 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.30 (hexane/AcOEt, 20/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.12−0.37 (m, 4H), 0.45−0.65 (m, 4H), 0.85 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H), 1.20−1.46 (m, 4H), 1.67−1.80 (m, 2H), 1.81−2.08 (m, 4H), 3.81 (s, 6H), 5.09−5.19 (m, 2H), 5.72−5.79 (m, 1H), 5.80−5.86 (m, 1H), 6.85−6.93 (m, 2H), 6.94−7.05 (m, 2H), 7.11−7.35 (m, 12H), 7.37−7.47 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.79 (CH_2), 1.82 (CH_2), 2.0 (CH_2), 2.1 (CH_2), 13.80 (CH_3), 13.85 (CH_3), 20.0 (CH), 20.5 (CH), 22.68 (CH_2), 22.71 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 32.9 (CH_3, both isomers), 47.9 (C, both isomers), 93.3 (CH), 93.4 (CH), 98.3 (CH), 98.7 (CH), 109.1 (CH), 109.2 (CH), 118.4 (CH), 118.5 (CH), 120.9 (C, both isomers), 121.1 (CH), 121.2 (CH), 121.8 (CH), 121.9 (CH), 126.1 (CH, both isomers), 126.8 (C), 127.0 (C), 127.4 (2 × CH), 127.5 (2 × CH), 127.8 (CH), 128.0 (CH), 128.8 (2 × CH), 129.1 (2 × CH), 137.70 (C), 137.73 (C), 144.8 (C), 145.5 (C), 203.7 (C), 203.9 (C). LRMS (70 eV, EI): m/z (%) 341 (M^+, 61), 260 (100). HRMS: calcd for $C_{25}H_{27}N$, 341.2144; found, 341.2147.

*3-(1,1-Diphenylhepta-2,3-dien-1-yl)-1-methyl-1H-indole (**1b**).* Colorless oil; yield = 70% (264 mg); R_f = 0.16 (hexane/diethyl ether, 20/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.73 (t, J = 7.3 Hz, 3H), 1.03−1.25 (m, 2H), 1.72−1.96 (m, 2H), 3.69 (s, 3H), 5.01 (dt, J = 7.6, 6.4 Hz, 1H), 6.18 (ddd, J = 6.4, 3.0, 2.6 Hz, 1H), 6.34 (s, 1H), 6.92−6.99 (m, 1H), 7.17−7.36 (m, 13H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.6 (CH_3), 22.6 (CH_2), 31.0 (CH_2), 32.8 (CH_3), 54.4 (C), 94.0 (CH), 99.7 (CH), 109.2 (CH), 118.6 (CH), 121.3 (CH), 121.4 (C), 122.9 (CH), 126.2 (2 × CH), 127.4 (C), 127.62 (2 × CH), 127.65 (2 × CH), 129.49 (CH), 129.52 (2 × CH), 129.6 (2 × CH), 137.8 (C), 146.3 (C), 146.6 (C), 204.1 (C). LRMS (70 eV, EI): m/z (%) 377 (M^+, 28), 334 (34), 296 (100). HRMS: calcd for $C_{28}H_{27}N$, 377.2144; found, 377.2136.

*3-(1,1-Dicyclopropylhepta-2,3-dien-1-yl)-1-methyl-1H-indole (**1c**).* Colorless liquid; yield = 65% (198 mg); R_f = 0.17 (hexane/AcOEt, 100/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.26−0.52 (m, 8H), 0.91 (t, J = 7.4 Hz, 3H), 1.23−1.49 (m, 4H), 1.91−2.13 (m, 2H), 3.76 (s, 3H), 5.11−5.25 (m, 2H), 7.02−7.10 (m, 1H), 7.04 (s, 1H), 7.14−7.23 (m, 1H), 7.24−7.30 (m, 1H), 7.88−7.95 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.2 (CH_2), 1.3 (CH_2), 1.9 (CH_2), 2.0 (CH_2), 13.8 (CH_3), 19.1 (CH), 19.4 (CH), 22.9 (CH_2), 31.4 (CH_2), 32.7 (CH_3), 42.2 (C), 92.6 (CH), 96.4 (CH), 109.2 (CH), 118.3 (CH), 119.5 (C), 121.0 (CH), 122.2 (CH), 127.6 (C), 127.7 (CH), 137.4 (C), 204.4 (C). LRMS (70 eV, EI): m/z (%) 305 (M^+, 64), 276 (35), 248 (69), 234 (42), 224 (100), 144 (64). HRMS: calcd for $C_{22}H_{27}N$, 305.2144; found, 305.2143.

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*3-(2-Cyclopropylocta-3,4-dien-2-yl)-1-methyl-1H-indole (**1d**).* Yellow liquid; yield = 70% (195 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.38 (hexane/diethyl ether, 50/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.30−0.54 (m, 8H), 0.91 (t, *J* = 7.4 Hz, 6H), 1.27−1.50 (m, 6H), 1.42 (s, 3H), 1.43 (s, 3H), 1.93−2.09 (m, 4H), 3.74 (s, 6H), 5.15−5.27 (m, 4H), 6.98 (s, 1 H), 6.99 (s, 1H), 7.01−7.09 (m, 2H), 7.15−7.23 (m, 2H), 7.24−7.30 (m, 2H), 7.77−7.87 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.39 (CH_2), 1.43 (CH_2), 1.68 (CH_2), 1.74 (CH_2), 13.9 (CH_3, both isomers), 21.6 (CH, both isomers), 22.8 (CH_2), 22.9 (CH_2), 25.6 (CH_3), 25.7 (CH_3), 31.5 (CH_2), 31.6 (CH_2), 32.7 (CH_3, both isomers), 38.4 (C, both isomers), 92.98 (CH), 93.0 (CH), 98.0 (CH), 98.3 (CH), 109.3 (CH, both isomers), 118.39 (CH), 118.43 (CH), 121.2 (CH, both isomers), 121.7 (CH, both isomers), 122.7 (C), 122.8 (C), 125.8 (CH), 125.9 (CH), 126.9 (C, both isomers), 137.8 (C, both isomers), 203.2 (C, both isomers). LRMS (70 eV, EI): *m*/*z* (%) 279 (M^+, 32), 222 (28), 198 (100). HRMS: calcd for $C_{20}H_{25}N$, 279.1987; found, 279.1985.

*1-Methyl-3-(2-methylocta-3,4-dien-2-yl)-1H-indole (**1e**).* Colorless oil; yield = 69% (175 mg); R_f = 0.24 (hexane/diethyl ether, 80/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.38−1.55 (m, 2H), 1.54 (s, 3H), 1.55 (s, 3H), 1.99−2.12 (m, 2H), 3.75 (s, 3H), 5.27 (aq, *J* = 6.6 Hz, 1H), 5.45 (dt, *J* = 6.6, 3.0 Hz, 1H), 6.85 (s, 1H), 7.06−7.15 (m, 1H), 7.18−7.26 (m, 1H), 7.27−7.34 (m, 1H), 7.78−7.86 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.9 (CH_3), 22.8 (CH_2), 29.1 (CH_3), 29.3 (CH_3), 31.5 (CH_2), 32.7 (CH_3), 35.3 (C), 93.5 (CH), 102.1 (CH), 109.4 (CH), 118.4 (CH), 121.3 (CH), 121.5 (CH), 123.5 (C), 124.9 (CH), 126.5 (C), 137.8 (C), 201.7 (C). LRMS (70 eV, EI): *m*/*z* (%) 253 (M^+, 29), 172 (100). HRMS: calcd for $C_{18}H_{23}N$, 253.1830; found, 253.1829.

*3-(1-Cyclopropyl-1-phenylpenta-2,3-dien-1-yl)-1-methyl-1H-indole (**1f**).* Colorless oil; yield = 74% (232 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.53 (hexane/diethyl ether, 20/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.14−0.36 (m, 4H), 0.47−0.62 (m, 4H), 1.57 (dd, *J* = 7.0, 3.2 Hz, 3H), 1.61−1.77 (m, 2H), 1.66 (dd, *J* = 7.0, 3.2 Hz, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 5.06−5.17 (m, 2H), 5.72 (td, *J* = 6.3, 3.1 Hz, 1H), 5.78 (td, *J* = 6.3, 3.1 Hz, 1H), 6.83−6.91 (m, 2H), 6.97−7.05 (m, 2H), 7.09−7.34 (m, 12H), 7.34−7.46 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.67 (CH_2), 1.74 (CH_2), 1.9 (CH_2), 2.0 (CH_2), 14.3 (CH_3), 14.6 (CH_3), 19.9 (CH), 20.5 (CH), 32.8 (CH_3, both isomers), 47.9 (C, both isomers), 88.0 (CH), 88.1 (CH), 98.0 (CH), 98.2 (CH), 109.1 (CH), 109.2 (CH), 118.46 (CH), 118.50 (CH), 120.7 (C), 121.1 (C), 121.16 (CH), 121.22 (CH), 121.8 (CH), 122.0 (CH), 126.08 (CH), 126.13 (CH), 126.7 (C), 127.0 (C), 127.4 (2 × CH), 127.5 (2 × CH), 127.7 (CH), 128.1 (CH), 128.8 (2 × CH), 129.1 (2 × CH), 137.66 (C), 137.72 (C), 144.7 (C), 145.4 (C), 204.6 (C), 204.8 (C). LRMS (70 eV, EI): *m*/*z* (%) 313 (M^+, 59), 270 (31), 260 (100). HRMS: calcd for $C_{23}H_{23}N$, 313.1830; found, 313.1830.

*3-(1-(4-Chlorophenyl)-1-cyclopropylpenta-2,3-dien-1-yl)-1-methyl-1H-indole (**1g**).* Colorless oil; yield = 89% (309 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.36 (hexane/diethyl ether, 30/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.13−0.25 (m, 3H), 0.26−0.34 (m, 1H), 0.46−0.62 (m, 4H), 1.55 (dd, *J* = 7.0, 3.2 Hz, 3H), 1.59−1.71 (m, 2H), 1.63 (dd, *J* = 7.0, 3.2 Hz, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 5.04−5.16 (m, 2H), 5.59−5.65 (m, 1H), 5.66−5.72 (m, 1H), 6.86−6.93 (m, 2H), 6.94−7.04 (m, 2H), 7.12 (s, 2H), 7.13−7.23 (m, 6H), 7.26−7.36 (m, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.7 (CH_2), 1.8 (CH_2), 1.9 (CH_2), 2.0 (CH_2), 14.2 (CH_3), 14.5 (CH_3), 20.1 (CH), 20.6 (CH), 32.9 (CH_3, both isomers), 47.6 (C, both isomers), 88.27 (CH), 88.35 (CH), 97.4 (CH), 97.7 (CH), 109.27 (CH), 109.32 (CH), 118.6 (CH), 118.7 (CH), 120.3 (C), 120.6 (C), 121.3 (CH), 121.4 (CH), 121.7 (CH), 121.8 (CH), 126.5 (C), 126.8 (C), 127.5 (2 × CH), 127.6 (2 × CH), 127.7 (CH), 128.0 (CH), 130.3 (2 × CH), 130.6 (2 × CH), 131.8 (C), 131.9 (C), 137.7 (C), 137.84(C), 143.5 (C), 144.1 (C), 204.7 (C), 204.9 (C). LRMS (70 eV, EI): *m*/*z* (%) 349 [$(M + 2)^+$, 19], 348 [$(M + 1)^+$, 17], 347 (M^+, 57), 294 (100). HRMS: calcd for $C_{23}H_{22}NCl$, 347.1441; found, 347.1455.

*1-Methyl-3-(2-methyl-3-phenylhepta-4,5-dien-3-yl)-1H-indole (**1h**).* Yellow oil; yield = 78% (246 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.24 (hexane/diethyl ether, 30/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.91 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 1.56 (dd, *J* = 7.0, 3.3 Hz, 3H), 1.60 (dd, *J* = 7.0, 3.3 Hz, 3H), 2.76−2.96 (m, 2H), 3.79 (s, 3H), 3.79 (s, 3H), 5.01−5.15 (m, 2H), 5.59−5.67 (m, 2H), 6.84−6.92 (m, 2H), 6.98−7.32 (m, 14H), 7.37−7.47 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.2 (CH_3), 14.5 (CH_3), 19.19 (CH_3), 19.21 (CH_3), 19.4 (CH_3), 19.5 (CH_3), 32.9 (CH_3, both isomers), 34.0 (CH), 34.6 (CH), 52.4 (C), 52.5 (C), 88.0 (CH), 88.1 (CH), 98.2 (CH), 98.5 (CH), 108.97 (CH), 109.02 (CH), 118.2 (CH), 118.3 (CH), 119.8 (C), 120.0 (C), 121.08 (CH), 121.09 (CH), 122.6 (CH), 122.9 (CH), 125.75 (CH), 121.79 (CH), 127.2 (2 × CH), 127.3 (2 × CH + C), 127.5 (C), 127.7 (CH), 127.9 (CH), 129.2 (2 × CH), 129.5 (2 × CH), 137.50 (C), 137.51 (C), 143.9 (C), 144.3 (C), 204.0 (C), 204.3 (C). LRMS (70 eV, EI): *m*/*z* (%) 315 (M^+, 17), 272 (100). HRMS: calcd for $C_{23}H_{25}N$, 315.1987; found, 315.1988.

*3-(1-Cyclopropyl-5-methyl-1-phenylhexa-2,3-dien-1-yl)-1-methyl-1H-indole (**1i**).* Colorless oil; yield = 65% (222 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.41 (hexane/diethyl ether, 50/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.02−0.14 (m, 1H), 0.12−0.33 (m, 3H), 0.40−0.62 (m, 4H), 0.86 (dd, *J* = 6.7, 1.0 Hz, 3H), 0.90 (dd, *J* = 6.7, 1.0 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 6H), 1.66−1.79 (m, 2H), 2.12−2.34 (m, 2H), 3.80 (s, 6H), 5.13 (tdd, *J* = 6.2, 3.3, 1.0 Hz, 1H), 5.77 (ddd, *J* = 6.2, 2.9, 1.0 Hz, 1H), 5.91 (ddd, *J* = 6.2, 2.9, 1.0 Hz, 1H), 6.80−6.95 (m, 4H), 7.08−7.30 (m, 12H), 7.32−7.44 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.2 (CH_2), 1.8 (CH_2), 2.0 (CH_2), 2.3 (CH_2), 19.7 (CH), 20.2 (CH), 22.4 (2 × CH_3), 22.78 (CH_3), 22.81 (CH_3), 28.47 (CH), 28.51 (CH), 32.9 (CH_3, both isomers), 48.0 (C, both isomers), 99.9 (CH), 100.3 (CH), 100.9 (CH), 101.1 (CH), 109.1 (CH), 109.2 (CH), 118.46 (CH), 118.49 (CH), 120.7 (C), 121.1 (CH), 121.2 (CH), 121.3 (C), 121.7 (CH), 121.9 (CH), 126.07 (CH), 126.12 (CH), 126.7 (C), 127.0 (C), 127.4 (2 × CH), 127.5 (2 × CH), 127.6 (CH), 128.1 (CH), 128.9 (2 × CH), 129.3 (2 × CH), 137.65 (C), 137.71 (C), 144.4 (C), 144.5 (C), 201.9 (C), 202.1 (C). LRMS (70 eV, EI): *m*/*z* (%) 341 (M^+, 31), 298 (77), 260 (100). HRMS: calcd for $C_{25}H_{27}N$, 341.2144; found, 341.2146.

*3-(1-Cyclopropyl-1,4-diphenylbuta-2,3-dien-1-yl)-1-methyl-1H-indole (**1j**).* White solid; yield = 60% (225 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.22 (hexane/AcOEt, 20/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.09−0.35 (m, 4H), 0.41−0.52 (m, 1H), 0.52−0.65 (m, 3H), 1.75−1.90 (m, 2H), 3.83 (s, 3H), 3.85 (s, 3H), 6.27 (d, *J* = 6.3 Hz, 1H), 6.33 (d, *J* = 6.3 Hz, 1H), 6.37 (d, *J* = 6.3 Hz, 1H), 6.43 (d, *J* = 6.3 Hz, 1H), 6.87−7.05 (m, 4H), 7.16−7.40 (m, 22H), 7.41−7.47 (m, 2H), 7.48−7.54 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.6 (CH_2), 1.8 (CH_2), 1.9 (CH_2), 2.0 (CH_2), 19.6 (CH), 19.8 (CH), 32.90 (CH_3), 32.93 (CH_3), 48.7 (C), 48.8 (C), 97.1 (CH), 97.2 (CH), 103.76 (CH), 103.82 (CH), 109.3 (CH, both isomers), 118.68 (CH), 118.71 (CH), 120.3 (C), 120.6 (C), 121.3 (CH, both isomers), 121.6 (CH), 121.7 (CH), 126.36 (CH), 126.39 (CH), 126.68 (C), 126.75 (3 × CH + C), 126.8 (2 × CH), 127.56 (2 × CH), 127.63 (2 × CH), 128.0 (CH), 128.1 (CH), 128.6 (2 × CH), 128.7 (2 × CH), 129.08 (2 × CH), 129.13 (2 × CH), 135.07 (C), 135.13 (C), 135.5 (C, both isomers), 137.7 (C), 137.8 (C), 144.1 (C), 144.2 (C), 205.0 (C), 205.3 (C). LRMS (70 eV, EI): *m*/*z* (%) 375 (M^+, 63), 347 (74), 260 (100). HRMS: calcd for $C_{28}H_{25}N$, 375.1987; found, 375.1974.

*1-Methyl-3-(1,1,4-triphenylbuta-2,3-dien-1-yl)-1H-indole (**1k**).* Pale-yellow solid; yield = 59% (242 mg); R_f = 0.22 (hexane/diethyl ether, 20/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.69 (s, 3H), 6.14 (d, *J* = 6.4 Hz, 1H), 6.44 (s, 1H), 6.68 (d, *J* = 6.4 Hz, 1H), 6.91−6.99 (m, 1H), 7.16−7.41 (m, 18H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 32.8 (CH_3), 54.9 (C), 97.7 (CH), 104.2 (CH), 109.3 (CH), 118.8 (CH), 121.0 (C), 121.5 (CH), 122.6 (CH), 126.4 (2 × CH), 126.8 (CH), 127.0 (2 × CH), 127.2 (C), 127.7 (2 × CH), 127.8 (2 × CH), 128.5 (2 × CH), 129.4 (2 × CH), 129.5 (CH), 129.7 (2 × CH), 134.6 (C), 137.9 (C), 145.8 (C), 146.3 (C), 205.5 (C). LRMS (70 eV, EI): *m*/*z* (%) 411 (M^+, 78), 296 (100). HRMS: calcd for $C_{31}H_{25}N$, 411.1987; found, 411.1986.

*3-(1-Cyclopropyl-1,4-diphenylpenta-2,3-dien-1-yl)-1-methyl-1H-indole (**1l**).* White foam; yield = 47% (366 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.22 (hexane/diethyl ether, 40/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.08−0.31 (m, 4H), 0.39−0.59 (m, 4H), 1.67−1.82 (m, 2H), 2.00 (d, *J* = 2.9 Hz, 3H), 2.13 (d, *J* = 2.9 Hz, 3H), 3.79 (s, 3H), 3.83 (s, 3H), 6.13−6.24 (m, 2H), 6.80−6.99 (m, 4H),

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7.10−7.42 (m, 24H), 7.43−7.49 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.6 (CH_2), 1.7 (CH_2), 1.9 (CH_2, both isomers), 17.2 (CH_3), 17.3 (CH_3), 19.7 (CH), 20.0 (CH), 32.8 (CH_3), 32.9 (CH_3), 48.8 (C), 49.0 (C), 101.45 (CH), 101.50 (CH), 102.9 (C), 103.0 (C), 109.2 (CH), 109.3 (CH), 118.5 (CH), 118.6 (CH), 120.3 (C), 121.16 (C), 121.19 (CH), 121.3 (CH), 121.7 (CH), 121.8 (CH), 125.6 (2 × CH), 125.7 (2 × CH), 126.2 (CH), 126.3 (CH), 126.4 (CH), 126.5 (CH), 126.7 (C), 126.9 (C), 127.5 (2 × CH), 127.6 (2 × CH), 127.8 (CH), 128.1 (CH), 128.3 (2 × CH, both isomers), 128.8 (2 × CH), 129.2 (2 × CH), 137.6 (C, both isomers), 137.7 (C, both isomers), 144.1 (C), 145.2 (C), 204.1 (C), 204.2 (C). LRMS (70 eV, EI): *m*/*z* (%) 389 (M^+, 62), 260 (100). HRMS: calcd for $C_{29}H_{27}N$, 389.2144; found, 389.2148.

3-(1-Cyclopropyl-1,4,4-triphenylbuta-2,3-dien-1-yl)-1-methyl-1H-indole (**1m**). White foam; yield = 50% (451 mg); R_f = 0.19 (hexane/diethyl ether, 40/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07−0.18 (m, 1H), 0.19−0.29 (m, 1H), 0.42−0.62 (m, 2H), 1.76−1.88 (m, 1H), 3.79 (s, 3H), 6.39 (s, 1H), 6.73−6.81 (m, 1H), 6.83−6.90 (m, 1H), 7.07−7.15 (m, 1H), 7.16 (s, 1H), 7.17−7.46 (m, 16H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 2.0 (CH_2), 2.2 (CH_2), 20.1 (CH), 32.9 (CH_3), 49.2 (C), 102.6 (CH), 109.2 (CH), 112.0 (C), 118.6 (CH), 120.4 (C), 121.3 (CH), 121.8 (CH), 126.3 (CH), 126.8 (C), 127.0 (CH), 127.1 (CH), 127.6 (2 × CH), 128.1 (CH), 128.3 (2 × CH), 128.4 (4 × CH), 128.5 (2 × CH), 129.0 (2 × CH), 137.2 (C), 137.3 (C), 137.7 (C), 144.6 (C), 205.4 (C). LRMS (70 eV, EI): *m*/*z* (%) 451 (M^+, 81), 308 (51), 260 (100). HRMS: calcd for $C_{34}H_{29}N$, 451.2300; found, 451.2302.

3-(1-Cyclopropyl-1-phenylbuta-2,3-dien-1-yl)-1-methyl-1H-indole (**1n**). Colorless oil; yield = 51% (153 mg); R_f = 0.29 (hexane/AcOEt, 50/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.13−0.32 (m, 2H), 0.49−0.65 (m, 2H), 1.69−1.82 (m, 1H), 3.82 (s, 3H), 4.71−4.85 (m, 2H), 5.88 (at, *J* = 6.6 Hz, 1H), 6.84−6.94 (m, 1H), 6.97−7.02 (m, 1H), 7.14−7.34 (m, 5H), 7.17 (s, 1H), 7.38−7.45 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.8 (CH_2), 1.9 (CH_2), 20.0 (CH), 32.9 (CH_3), 47.5 (C), 77.3 (CH_2), 98.4 (CH), 109.2 (CH), 118.6 (CH), 120.6 (C), 121.3 (CH), 121.7 (CH), 126.3 (CH), 126.8 (C), 127.5 (2 × CH), 128.0 (CH), 129.0 (2 × CH), 137.7 (C), 144.6 (C), 208.2 (C). LRMS (70 eV, EI): *m*/*z* (%) 299 (M^+, 81), 284 (54), 270 (88), 260 (100), 144 (48). HRMS: calcd for $C_{22}H_{21}N$, 299.1674; found, 299.1672.

1-Methyl-3-(2-phenylpenta-3,4-dien-2-yl)-1H-indole (**1o**). White solid; yield = 52% (142 mg); R_f = 0.18 (hexane/AcOEt, 50/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.87 (s, 3H), 3.79 (s, 3H), 4.81−4.93 (m, 2H), 5.94 (at, *J* = 6.6 Hz, 1H), 6.98 (s, 1H), 6.96−7.00 (s, 1H), 7.06−7.13 (m, 1H), 7.15−7.34 (m, 5H), 7.38−7.44 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.4 (CH_3), 32.9 (CH_3), 43.0 (C), 77.8 (CH_2), 100.0 (CH), 109.4 (CH), 118.7 (CH), 121.47 (CH), 121.49 (CH), 122.2 (C), 126.1 (CH), 126.2 (C), 126.6 (CH), 127.2 (2 × CH), 128.1 (2 × CH), 137.9 (C), 148.2 (C), 207.0 (C). LRMS (70 eV, EI): *m*/*z* (%) 273 (M^+, 65), 258 (100), 234 (64). HRMS: calcd for $C_{20}H_{19}N$, 273.1517; found, 273.1516.

3-(1-Cyclopropyl-1-(thiophen-2-yl)buta-2,3-dien-1-yl)-1-methyl-1H-indole (**1p**). White solid; yield = 75% (229 mg); R_f = 0.18 (hexane/diethyl ether, 30/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.32−0.47 (m, 2H), 0.53−0.65 (m, 2H), 1.74−1.83 (m, 1H), 3.78 (s, 3H), 4.72−4.81 (m, 2H), 5.76−5.83 (m, 1H), 6.89−6.93 (m, 2H), 6.94−6.99 (m, 1H), 7.08 (s, 1H), 7.15−7.20 (m, 2H), 7.24−7.31 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 2.5 (CH_2), 2.6 (CH_2), 21.7 (CH), 32.9 (CH_3), 45.7 (C), 77.9 (CH_2), 98.3 (CH), 109.3 (CH), 118.8 (CH), 120.1 (C), 121.4 (CH), 121.8 (CH), 123.8 (CH), 125.5 (CH), 126.1 (CH), 126.9 (C), 127.8 (CH), 137.6 (C), 151.5 (C), 208.1 (C). LRMS (70 eV, EI): *m*/*z* (%) 305 (M^+, 100), 266 (86). HRMS: calcd for $C_{23}H_{15}N$, 305.1238; found, 305.1233.

3-(1,1-Diphenylbuta-2,3-dien-1-yl)-1-methyl-1H-indole (**1q**). Yellow oil; yield = 46% (308 mg); R_f = 0.31 (hexane/diethyl ether, 30/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.69 (s, 3H), 4.66 (d, *J* = 6.6 Hz, 2H), 6.24 (t, *J* = 6.6 Hz, 1H), 6.32 (s, 1H), 6.93−7.02 (m, 1H), 7.16−7.38 (m, 13H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 32.8 (CH_3), 54.0 (C), 78.1 (CH_2), 99.5 (CH), 109.2 (CH), 118.7 (CH), 121.0 (C), 121.4 (CH), 122.7 (CH), 126.4 (2 × CH_2), 127.3 (C), 127.7 (4 × CH), 129.5 (4 × CH), 129.6 (CH), 137.8 (C), 146.1 (2 × C), 208.5 (C). LRMS (70 eV, EI): *m*/*z* (%) 335 (M^+, 68), 296 (100). HRMS: calcd for $C_{25}H_{21}N$, 335.1674; found, 335.1676.

3-(1,1-Dicyclopropylbuta-2,3-dien-1-yl)-1-methyl-1H-indole (**1r**). White solid; yield = 60% (158 mg); mp 56−58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.26−0.33 (m, 2H), 0.36−0.48 (m, 6H), 1.23−1.34 (m, 2H), 3.75 (s, 3H), 4.78 (d, *J* = 6.7 Hz, 2H), 5.19 (t, *J* = 6.7 Hz, 1H), 7.02 (s, 1H), 7.01−7.07 (m, 1H), 7.14−7.20 (m, 1H), 7.24−7.28 (m, 1H), 7.83−7.87 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.3 (2 × CH_2), 2.0 (2 × CH_2), 19.3 (2 × CH), 32.8 (CH_3), 42.1 (C), 76.5 (CH_2), 96.1 (CH), 109.3 (CH), 118.5 (CH), 119.2 (C), 121.1 (CH), 122.2 (CH), 127.7 (C), 127.8 (CH), 137.4 (C), 208.8 (C). LRMS (70 eV, EI): *m*/*z* (%) 263 (M^+, 54), 234 (100), 224 (64), 220 (66), 144 (54). HRMS: calcd for $C_{19}H_{21}N$, 263.1674; found, 263.1674.

3-(1-(4-Chlorophenyl)hepta-2,3-dien-1-yl)-1-methyl-1H-indole (**1s**). Yellow oil; yield = 47% (315 mg); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.28 (hexane/diethyl ether, 30/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, *J* = 7.3 Hz, 6H), 1.26−1.46 (m, 4H), 1.85−2.08 (m, 4H), 3.77 (s, 3H), 3.78 (s, 3H), 4.94−5.02 (m, 2H), 5.12−5.22 (m, 2H), 5.62−5.70 (m, 2H), 6.84−6.89 (m, 2H), 7.03−7.12 (m, 2H), 7.21−7.36 (m, 12H), 7.41−7.48 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.68 (CH_3), 13.71 (CH_3), 22.48 (CH_2), 22.54 (CH_2), 31.1 (CH_2, both isomers), 32.8 (CH_3, both isomers), 42.9 (CH), 43.0 (CH), 92.9 (CH), 93.0 (CH), 94.5 (CH), 94.6 (CH), 109.3 (CH, both isomers), 117.1 (C), 117.2 (C), 118.93 (CH), 118.95 (CH), 119.86 (CH), 119.88 (CH), 121.79 (CH), 121.81 (CH), 127.17 (CH), 127.22 (CH), 128.4 (2 × CH, both isomers), 129.7 (2 × CH, both isomers), 130.0 (C, both isomers), 131.9 (C, both isomers), 137.5 (C, both isomers), 142.6 (C, both isomers), 204.17 (C), 204.22 (C). LRMS (70 eV, EI): *m*/*z* (%) 337 [(M + 2)$^+$, 17], 336 [(M + 1)$^+$, 14], 335 (M^+, 52), 254 (100). HRMS: calcd for $C_{22}H_{22}NCl$, 335.1441; found, 335.1451.

3-(1-(4-Chlorophenyl)buta-2,3-dien-1-yl)-1-methyl-1H-indole (**1t**). Yellow oil; yield = 47% (275 mg); R_f = 0.27 (hexane/diethyl ether, 20/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.76 (s, 3H), 4.70−4.78 (m, 2H), 4.94−5.00 (m, 1H), 5.59−5.70 (m, 1H), 6.83 (s, 1H), 7.01−7.08 (m, 1H), 7.17−7.34 (m, 6H), 7.37−7.44 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 32.8 (CH_3), 42.4 (CH), 76.8 (CH_2), 94.0 (CH), 109.4 (CH), 116.8 (C), 119.1 (CH), 119.8 (CH), 121.9 (CH), 127.0 (C), 127.2 (CH), 128.5 (2 × CH), 129.7 (2 × CH), 132.1 (C), 137.5 (C), 142.2 (C), 208.5 (C). LRMS (70 eV, EI): *m*/*z* (%) 295 [(M + 2)$^+$, 28], 293 (M^+, 52), 256 (35), 254 (100). HRMS: calcd for $C_{19}H_{16}ClN$, 293.0971; found, 293.0973.

1-Methyl-3-(1-(naphthalen-1-yl)buta-2,3-dien-1-yl)-1H-indole (**1u**). Yellow oil; yield = 48% (297 mg); R_f = 0.32 (hexane/AcOEtr, 8/1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.77 (s, 3H), 4.82−4.91 (m, 2H), 5.23−5.33 (m, 1H), 5.83−5.93 (m, 1H), 6.89 (bs, 1H), 7.09−7.19 (m, 1H), 7.23−7.43 (m, 2H), 7.46−7.67 (m, 4H), 7.80−7.98 (m, 4H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 32.7 (CH_3), 43.2 (CH), 76.6 (CH_2), 94.1 (CH), 109.3 (CH), 117.3 (C), 119.0 (CH), 120.0 (CH), 121.7 (CH), 125.5 (CH), 125.9 (CH), 126.3 (CH), 127.16 (CH), 127.28 (C), 127.32 (CH), 127.7 (CH), 127.9 (2 × CH), 132.5 (C), 133.6 (C), 137.5 (C), 141.2 (C), 208.6 (C). HRMS: calcd for $C_{23}H_{19}N$, 309.1517; found, 309.1520.

1-Methyl-3-(4-phenylbuta-2,3-dien-1-yl)-1H-indole (**1v**). Yellow oil; yield = 46% (238 mg); R_f = 0.28 (hexane/diethyl ether, 20/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.68 (dd, *J* = 7.2, 2.6 Hz, 2H), 3.79 (s, 3H), 5.85 (dt, *J* = 6.4, 7.2 Hz, 1H), 6.27 (dt, *J* = 6.4, 2.6 Hz, 1H), 6.98 (s, 1H), 7.14−7.21 (m, 1H), 7.22−7.43 (m, 7H), 7.66−7.72 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 25.5 (CH_2), 32.7 (CH_3), 94.6 (CH), 95.0 (CH), 109.3 (CH), 113.2 (C), 118.9 (CH), 119.3 (CH), 121.8 (CH), 126.6 (CH), 126.86 (CH), 126.92 (2 × CH), 127.8 (C), 128.7 (2 × CH), 135.0 (C), 137.2 (C), 205.5 (C). LRMS (70 eV, EI): *m*/*z* (%) 259 (M^+, 36), 144 (100). HRMS: calcd for $C_{19}H_{17}N$, 259.1361; found, 259.1363.

Gold(I)-Catalyzed Synthesis of 4,9-Dihydro-1*H*-carbazoles 2 and 3. *Method A.* A mixture of $(PhO)_3PAuCl$ (5 mol %, 14 mg) and AgOTf (5 mol %, 7 mg) in dry toluene (0.5 mL) was stirred at room temperature for 5 min and then cooled to −78 °C. The corresponding allenylmethylindole **1** (0.5 mmol) in dry toluene (1 mL) was added, and the mixture was stirred while it was allowed to slowly reach rt, until the starting material was completely consumed (as determined by TLC or GC−MS analysis). After filtration through a short pad of Celite using CH_2Cl_2 as the eluent, the solvent was removed under reduced pressure,

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and the crude residue was purified by flash chromatography on deactivated silica gel using a hexane/diethyl ether or hexane/AcOEt mixture as the eluent to afford the corresponding 4,9-dihydro-1*H*-carbazoles **2** and/or **3** in the ratio reported in Table 2 and Scheme 3 and the yields depicted in Table 2 and Schemes 4 and 5. The minor regioisomer, if formed in a significant amount, was also isolated in the yields reported below. Both dihydrocarbazoles were obtained as ∼1/1 mixtures of diastereomers and isolated as variable mixtures of them [notated as maj (major) and min (minor) in the NMR data].

Method B. PPh_3AuNTf_2 (5 mol %, 18 mg) was added to a solution of the corresponding allenylmethylindole **1** (0.5 mmol) in dry CH_2Cl_2 (1.5 mL) at −78 °C. The resulting mixture was stirred while it was allowed to slowly reach rt, until the starting material was completely consumed (as determined by TLC or GC−MS analysis). After filtration through a short pad of Celite using CH_2Cl_2 as the eluent, the solvent was removed under reduced pressure, and the crude residue was purified by flash chromatography on deactivated silica gel using a hexane/diethyl ether or hexane/AcOEt mixture as the eluent to afford the corresponding 4,9-dihydro-1*H*-carbazoles **2** and/or **3** in the ratio reported in Table 3 and Scheme 3 and the yields depicted in Table 3 and Schemes 4 and 5. The minor regioisomer, if formed in significant amount, was also isolated in the yields reported below. Both dihydrocarbazoles were obtained as ∼1/1 mixtures of diastereomers and isolated as variable mixtures of them [notated as maj (major) and min (minor) in the NMR data].

Spectroscopic and Characterization Data for 4,9-Dihydro-1*H*-carbazoles 2 and 3. *4-Cyclopropyl-9-methyl-4-phenyl-1-propyl-4,9-dihydro-1H-carbazole (**2a**).* Colorless oil; yield = 78% (133 mg) (method A); isolated as a ∼1/2.3 mixture of diastereoisomers; R_f = 0.16 (hexane/AcOEt, 40/1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.06−0.29 (m, 3H), 0.39−0.53 (m, 1H), 0.64−0.79 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 3H, maj), 1.05 (t, *J* = 7.1 Hz, 3H, min), 1.26−1.98 (m, 10H), 3.58−3.69 (m, 2H, both isomers), 3.74 (s, 3H, min), 3.77 (s, 3H, maj), 5.49 (dd, *J* = 10.1, 2.0 Hz, 1H, maj), 5.52 (dd, *J* = 10.0, 1.4 Hz, 1H, min), 5.88 (dd, *J* = 10.1, 3.6 Hz, 1H, maj), 6.04 (dd, *J* = 10.0, 4.2 Hz, 1H, min), 6.75−6.82 (m, 1H, min), 6.83−6.90 (m, 1H, maj), 6.93−6.99 (m, 1H, min), 7.01−7.36 (m, 11H), 7.49−7.65 (m, 4H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 1.0 (CH_2, maj), 2.5 (CH_2, min), 2.6 (CH_2, min), 3.0 (CH_2, maj), 14.1 (CH_3, both isomers), 19.2 (CH, maj), 19.4 (CH_2, min), 20.2 (CH, min), 20.8 (CH_2, maj), 30.1 (CH_3, min), 30.5 (CH_3, maj), 33.26 (CH, maj), 33.34 (CH, min), 38.1 (CH_2, maj), 39.9 (CH_2, min), 45.8 (C, maj), 46.3 (C, min), 108.78 (CH, min), 108.82 (CH, maj), 113.0 (C, min), 114.2 (C, maj), 118.5 (CH, both isomers), 119.8 (CH, min), 120.0 (CH, maj), 120.5 (CH, min), 120.6 (CH, maj), 125.4 (C, maj), 125.6 (C, min), 125.76 (CH, min), 125.84 (CH, maj), 126.3 (CH, min) 127.5 (CH, maj), 127.80 (2 × CH, min), 127.83 (2 × CH, maj), 127.99 (2 × CH, maj), 128.04 (2 × CH, min), 130.5 (CH, maj), 132.4 (CH, min), 136.6 (C, both isomers), 137.6 (C, min), 137.8 (C, maj), 148.4 (C, maj), 148.8 (C, min). LRMS (70 eV, EI): isomer 1: *m*/*z* (%) 341 (M^+, 67), 300 (100), 257 (93); isomer 2: *m*/*z* (%) 341 (M^+, 78), 300 (72), 270 (100), 257 (94). HRMS: calcd for $C_{25}H_{27}N$, 341.2144; found, 341.2143.

*1-Cyclopropyl-9-methyl-1-phenyl-4-propyl-4,9-dihydro-1H-carbazole (**3a**).* Colorless oil; yield = 68% (116 mg) (method B); isolated as a ∼1/1.3 mixture of diastereoisomers; R_f = 0.25 (hexane/AcOEt, 40/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.07−0.15 (m, 1H), 0.28−0.38 (m, 2H), 0.40−0.50 (m, 1H), 0.75−0.89 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 3H, maj), 1.05 (t, *J* = 7.3 Hz, 3H, min), 1.30−1.44 (m, 2H), 1.50−1.82 (m, 5H), 1.92−2.12 (m, 2H), 2.15−2.27 (m, 1H), 3.32 (s, 3H, min), 3.36 (s, 3H, maj), 3.75−3.85 (m, 2H, both isomers), 5.28−5.31 (m, 1H, maj), 5.31−5.33 (m, 1H, min), 5.90 (dd, *J* = 10.0, 3.0 Hz, 1H, maj), 6.02 (dd, *J* = 10.0, 3.9 Hz, 1H, min), 7.14−7.40 (m, 14H, both isomers), 7.48−7.53 (m, 2H, both isomers), 7.70−7.77 (m, 2H, both isomers). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 0.9 (CH_2, maj), 1.5 (CH_2, min), 3.1 (CH_2, min), 3.2 (CH_2, maj), 14.6 (CH_3, both isomers), 18.6 (CH, min), 19.1 (CH_2, maj), 19.4 (CH, maj), 20.3 (CH_2, min), 31.4 (CH_3, min), 31.5 (CH_3, maj), 34.3 (CH, maj), 34.5 (CH, min), 37.8 (CH_2, maj), 39.8 (CH_2, min), 45.4 (C, maj), 45.6 (C, min), 108.9 (CH, both isomers), 111.5 (C, maj), 112.2 (C, min), 118.7 (CH, maj), 118.8 (CH, min), 119.1 (CH, min), 119.4 (CH, maj), 121.0 (CH, maj), 121.1 (CH, min), 125.8 (C, min), 125.9 (C, maj), 126.42 (CH, min), 126.45 (CH, maj), 127.5 (2 × CH, maj), 127.6 (2 × CH, min), 128.6 (2 × CH, min), 128.7 (2 × CH, maj), 128.9 (CH, maj), 129.0 (CH, min), 129.2 (CH, min), 129.6 (CH, maj), 137.7 (C, min), 137.8 (C, maj), 138.4 (C, min), 138.7 (C, maj), 147.4 (C, min), 147.5 (C, maj). LRMS (70 eV, EI): isomer 1: *m*/*z* (%) 341 (M^+, 16), 298 (100), 257 (48); isomer 2: *m*/*z* (%) 341 (M^+, 17), 298 (100), 257 (49). HRMS: calcd for $C_{25}H_{27}N$, 341.2144; found, 341.2162.

*9-Methyl-4,4-diphenyl-1-propyl-4,9-dihydro-1H-carbazole (**2b**).* White solid; yield = 91% (171 mg) (method A); mp = 171−173 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.88 (t, *J* = 7.3 Hz, 3H), 1.19−1.35 (m, 2H), 1.58−1.73 (m, 1H), 1.77−1.92 (m, 1H), 3.69−3.83 (m, 1H), 3.78 (s, 3H), 6.06 (dd, *J* = 9.9, 4.2 Hz, 1H), 6.26 (dd, *J* = 9.8, 1.5 Hz, 1H), 6.77−6.86 (m, 1H), 6.99−7.39 (m, 13H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 14.0 (CH_3), 19.3 (CH_2), 30.1 (CH_3), 33.3 (CH), 37.8 (CH_2), 52.4 (C), 108.8 (CH), 113.0 (C), 118.7 (CH), 120.4 (CH), 120.7 (CH), 125.1 (CH), 125.8 (CH), 126.0 (CH), 126.1 (C), 127.6 (2 × CH), 127.9 (2 × CH), 129.0 (2 × CH), 129.1 (2 × CH), 136.6 (CH), 137.3 (C), 137.7 (C), 145.9 (C), 147.7 (C). LRMS (70 eV, EI): *m*/*z* (%) 377 (M^+, 49), 335 (28), 334 (100), 300 (37), 257 (33). HRMS: calcd for $C_{28}H_{27}N$, 377.2144; found, 377.2152.

*9-Methyl-1,1-diphenyl-4-propyl-4,9-dihydro-1H-carbazole (**3b**).* White solid; yield = 20% (38 mg) (method B); mp = 160−162 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.87 (t, *J* = 7.4 Hz, 3H), 1.20−1.32 (m, 2H), 1.75−1.87 (m, 1H), 1.91−2.02 (m, 1H), 3.12 (s, 3H), 3.85−3.93 (m, 1H), 5.96 (dd, *J* = 9.8, 3.6 Hz, 1H), 6.04 (dd, *J* = 9.8, 1.4 Hz, 1H), 7.07−7.13 (m, 1H), 7.14−7.39 (m, 12H), 7.67−7.73 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 14.2 (CH_3), 19.4 (CH_2), 31.7 (CH_3), 34.2 (CH), 38.1 (CH_2), 51.8 (C), 108.9 (CH), 112.4 (C), 118.8 (CH), 119.2 (CH), 121.3 (CH), 125.7 (C), 126.0 (CH), 126.4 (CH), 126.5 (CH), 128.1 (2 × CH), 128.3 (2 × CH), 129.1 (2 × CH), 129.3 (2 × CH), 135.2 (CH), 137.1 (C), 137.6 (C), 143.7 (C), 144,7 (C). LRMS (70 eV, EI): *m*/*z* (%) 377 (M^+, 44), 335 (81), 334 (100), 319 (32), 257 (39). HRMS: calcd for $C_{28}H_{27}N$, 377.2144; found, 377.2138.

*4,4-Dicyclopropyl-9-methyl-1-propyl-4,9-dihydro-1H-carbazole (**2c**).* White solid; yield = 57% (87 mg) (method A); mp = 101−103 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.18−0.45 (m, 6H), 0.48−0.56 (m, 1H), 0.71−0.80 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H), 1.23−1.32 (m, 1H), 1.34−1.61 (m, 4H), 1.82−1.93 (m, 1H), 3.45−3.52 (m, 1H), 3.69 (s, 3H), 5.46 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.94 (dd, *J* = 10.2, 4.0 Hz, 1H), 7.01−7.08 (m, 1H), 7.11−7.17 (m, 1H), 7.27−7.32 (m, 1H), 7.84−7.89 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 0.6 (CH_2), 1.3 (CH_2), 1.5 (CH_2), 2.2 (CH_2), 14.1 (CH_3), 19.3 (CH), 19.6 (CH_2), 20.5 (CH), 30.1 (CH_3), 33.5 (CH), 39.2 (CH_2), 40.4 (C), 108.9 (CH), 114.1 (C), 118.5 (CH), 120.4 (CH), 121.0 (CH), 126.1 (C), 127.7 (CH), 130.1 (CH), 136.6 (C), 137.6 (C). LRMS (70 eV, EI): *m*/*z* (%) 305 (M^+, 28), 264 (100), 221 (28). HRMS: calcd for $C_{22}H_{27}N$, 305.2144; found, 305.2138.

*4-Cyclopropyl-4,9-dimethyl-1-propyl-4,9-dihydro-1H-carbazole (**2d**).* Colorless oil; yield = 64% (89 mg) (method A); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.26 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.15−0.35 (m, 4H), 0.38−0.55 (m, 3H), 0.59−0.68 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.97 (t, 7.2 Hz, 3H), 1.02−1.17 (m, 1H), 1.27−1.62 (m, 6H), 1.41 (s, 3H), 1.48 (s, 3H), 1.63−1.82 (m, 2H), 1.83−1.93 (m, 1H), 3.48−3.54 (m, 1H), 3.59−3.64 (m, 1H), 3.69 (s, 3H), 3.70 (s, 3H), 5.55−5.60 (m, 2H), 5.80 (dd, *J* = 10.1, 3.9 Hz, 1H), 5.90 (dd, *J* = 10.1, 4.2 Hz, 1H), 7.03−7.08 (m, 2H), 7.12−7.18 (m, 2H), 7.28−7.33 (m, 2H), 7.72−7.80 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 1.2 (CH_2), 1.5 (CH_2), 1.8 (CH_2), 1.9 (CH_2), 14.05 (CH_3), 14.08 (CH_3), 18.5 (CH_2), 19.6 (CH_2), 21.9 (CH), 22.1 (CH), 25.9 (CH_3), 26.6 (CH_3), 29.9 (CH_3), 30.2 (CH_3), 33.5 (2 × CH), 36.8 (C), 37.5 (CH_2), 37.6 (C), 39.4 (CH_2), 108.86 (CH), 108.94 (CH), 114.6 (C), 116.2 (C), 118.4 (CH), 118.5 (CH), 120.3 (CH), 120.4 (3 × CH), 125.6 (C), 125.7 (C), 125.9 (CH), 126.3 (CH), 133.7 (CH), 134.6 (CH), 135.4 (C), 136.4 (C), 137.6 (C), 137.7 (C). LRMS (70 eV, EI): *m*/*z* (%) 279 (M^+, 58), 264 (100), 238 (73), 195 (81). HRMS: calcd for $C_{20}H_{25}N$, 279.1987; found, 279.1996.

*4,4,9-Trimethyl-1-propyl-4,9-dihydro-1H-carbazole (**2e**).* Colorless oil; yield = 80% (101 mg) (method A); R_f = 0.25 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.88 (t, *J* = 7.4 Hz, 3H), 1.05−1.21 (m, 1H), 1.27−1.43 (m, 1H), 1.49 (s, 3H), 1.50 (s, 3H), 1.63−1.82 (m, 2H), 3.59−3.64 (m, 1H), 3.69 (s, 3H), 5.71−5.79 (m, 2H), 7.02−7.08 (m, 1H), 7.11−7.17 (m, 1H), 7.28−7.32 (m, 1H), 7.65−7.70 (m,

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1H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 14.1 (CH_3), 18.6 (CH_2), 29.8 (CH_3), 29.9 (CH_3), 30.0 (CH_3), 35.5 (CH), 34.7 (C), 37.7 (CH_2), 109.0 (CH), 116.0 (C), 118.4 (CH), 119.8 (CH), 120.4 (CH), 124.2 (CH), 125.4 (C), 135.2 (C), 137.7 (C), 138.6 (CH). LRMS (70 eV, EI): m/z (%) 253 (M^+, 21), 252 (76), 236 (53), 210 (100). HRMS: calcd for $C_{18}H_{23}N$, 253.1830; found, 253.1832.

*4-Cyclopropyl-1,9-dimethyl-4-phenyl-4,9-dihydro-1H-carbazole (**2f**).* Colorless oil; yield = 57% (89 mg) (method A); isolated as a ∼1/1.4 mixture of diastereoisomers; R_f = 0.28 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.16−0.84 (m, 2H), 0.36−0.53 (m, 2H), 0.64−0.81 (m, 3H, both isomers), 0.88−0.97 (m, 1H, min), 1.48 (d, J = 6.9 Hz, 3H, maj), 1.50 (d, J = 7.0 Hz, 3H, min), 1.80−1.90 (m, 1H, min), 1.94−2.05 (m, 1H, maj), 3.62−3.74 (m, 2H, both isomers), 3.76 (s, 3H, min), 3.78 (s, 3H, maj), 5.45 (dd, J = 10.0, 1.9 Hz, 1H, maj), 5.52 (dd, J = 9.9, 1.4 Hz, 1H, min), 5.85 (dd, J = 10.0, 3.7 Hz, 1H, maj), 5.92 (dd, J = 9.9, 4.2 Hz, 1H, min), 6.79−6.86 (m, 1H, min), 6.86−6.92 (m, 1H, maj), 6.96−7.01 (m, 1H, min), 7.06−7.25 (m, 6H, both isomers), 7.26−7.36 (m, 5H, both isomers), 7.55−7.65 (m, 4H, both isomers). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 1.2 (CH_2, maj), 2.5 (CH_2, min), 2.7 (CH_2, min), 2.9 (CH_2, maj), 19.5 (CH, min), 20.3 (CH, maj), 22.4 (CH_3, maj), 22.8 (CH_3, min), 28.5 (CH, maj), 28.6 (CH, min), 30.0 (CH_3, min), 30.4 (CH_3, maj), 46.0 (C, maj), 46.4 (C, min), 108.8 (CH, min), 108.9 (CH, maj), 112.5 (C, min), 113.2 (C, maj), 118.5 (CH, min), 118.6 (CH, maj), 120.0 (CH, min), 120.1 (CH, maj), 120.6 (CH, min), 120.7 (CH, maj), 125.4 (C, maj), 125.7 (C, min), 125.8 (CH, min), 125.9 (CH, maj), 127.87 (2 × CH, maj), 127.88 (2 × CH, min), 128.06 (2 × CH, maj), 128.10 (2 × CH, min), 128.4 (CH, min), 129.2 (CH, maj), 129.6 (CH, maj), 131.7 (CH, min), 137.6 (C, min), 137.78 (C, maj), 137.84 (C, maj), 138.2 (C, min), 148.4 (C, maj), 148.7 (C, min). LRMS (70 eV, EI): m/z (%) 313 (M^+, 58), 272 (100), 257 (47). HRMS: calcd for $C_{23}H_{23}N$, 313.1830; found, 313.1836.

*1-Cyclopropyl-4,9-dimethyl-1-phenyl-4,9-dihydro-1H-carbazole (**3f**).* Colorless oil; yield = 15% (24 mg) (method A), 24% (38 mg) (method B); isolated as a ∼1/1.1 mixture of diastereoisomers; R_f = 0.21 (hexane/diethyl ether, 200/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.05−0.14 (m, 1H, maj), 0.19−0.28 (m, 1H, min), 0.29−0.37 (m, 1H, maj), 0.37−0.47 (m, 1H, min), 0.74−0.93 (m, 4H, both isomers), 1.48 (d, J = 7.1 Hz, 3H, min), 1.50 (d, J = 7.1 Hz, 3H, maj), 1.70−1.80 (m, 2H, both isomers), 3.27 (s, 3H, min), 3.31 (s, 3H, maj), 3.69−3.84 (m, 2H, both isomers), 5.22 (dd, J = 9.9, 1.6 Hz, 1H, min), 5.23 (dd, J = 10.0, 2.1 Hz, 1H, maj), 5.83 (dd, J = 10.0, 3.1 Hz, 1H, maj), 5.89 (dd, J = 9.9, 3.9 Hz, 1H, min), 7.07−7.13 (m, 2H), 7.15−7.20 (m, 2H), 7.20−7.36 (m, 8H, both isomers), 7.36−7.42 (m, 2H), 7.42−7.48 (m, 2H), 7.61−7.70 (m, 2H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 0.5 (CH_2, maj), 1.0 (CH_2, min), 2.9 (CH_2, both isomers), 18.4 (CH, min), 19.0 (CH, maj), 22.5 (CH_3, maj), 23.0 (CH_3, min), 29.4 (CH, maj), 29.5 (CH, min), 31.2 (CH_3, min), 31.3 (CH_3, maj), 45.4 (C, maj), 45.5 (C, min), 108.8 (CH, both isomers), 112.86 (C, maj), 112.94 (C, min), 118.65 (CH, min), 118.70 (CH, maj), 118.8 (CH, min), 119.2 (CH, maj), 121.0 (CH, both isomers), 125.8 (C, both isomers), 126.3 (CH, both isomers), 127.50 (2 × CH, min), 127.53 (2 × CH, maj), 127.8 (CH, maj), 128.2 (CH, min), 128.5 (2 × CH, min), 128.6 (2 × CH, maj), 131.0 (CH, min), 131.2 (CH, maj), 137.6 (C, maj), 137.7 (C, min), 137.8 (C, maj), 137.9 (C, min), 147.2 (C, maj), 147.3 (C, min). LRMS (70 eV, EI): m/z (%) 313 (M^+, 80), 298 (100), 257 (61). HRMS: calcd for $C_{23}H_{23}N$, 313.1830; found, 313.1829.

*4-(4-Chlorophenyl)-4-cyclopropyl-1,9-dimethyl-4,9-dihydro-1H-carbazole (**2g**).* White solid; yield = 66% (115 mg) (method A); isolated as a ∼1/1 mixture of diastereoisomers; R_f = 0.20 (hexane/diethyl ether, 100/1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.10−0.34 (m, 2H), 0.35−0.54 (m, 2H), 0.60−0.82 (m, 3H), 0.83−0.99 (m, 1H), 1.46 (d, J = 6.9 Hz, 3H), 1.48 (d, J = 7.0 Hz, 3H), 1.73−1.86 (m, 1H), 1.87−1.99 (m, 1H), 3.60−3.75 (m, 2H), 3.76 (s, 3H), 3.78 (s, 3H), 5.39 (dd, J = 10.0, 1.9 Hz, 1H), 5.46 (dd, J = 9.9, 1.4 Hz, 1H), 5.85 (dd, J = 10.0, 3.7 Hz, 1H), 5.92 (dd, J = 9.9, 4.3 Hz, 1H), 6.80−6.86 (m, 1H), 6.87−6.93 (m, 1H), 6.94−6.98 (m, 1H), 7.05−7.17 (m, 3H), 7.22−7.36 (m, 6H), 7.47−7.60 (m, 4H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.3 (CH_2), 2.5 (CH_2), 2.7 (CH_2), 2.8 (CH_2), 19.5 (CH), 20.3 (CH), 22.4 (CH_3), 22.7 (CH_3), 28.5 (CH), 28.6 (CH), 30.0 (CH_3), 30.4 (CH_3), 45.7 (C), 46.1 (C), 108.87 (CH), 108.92 (CH), 112.0 (C), 112.8 (C), 118.7 (CH, both isomers), 119.9 (CH), 120.0 (CH), 120.7 (CH), 120.8 (CH), 125.2 (C), 125.4 (C), 127.9 (2 × CH), 128.1 (2 × CH), 128.8 (CH), 129.1 (CH), 129.4 (2 × CH), 129.6 (2 × CH), 129.7 (CH), 131.2 (CH), 131.4 (C), 131.5 (C), 137.6 (C), 137.8 (C), 137.9 (C), 138.3 (C), 147.2 (C), 147.4 (C). LRMS (70 eV, EI): m/z (%) 349 [$(M + 2)^+$, 21], 348 [$(M + 1)^+$, 16], 347 (M^+, 61), 306 (100). HRMS: calcd for $C_{23}H_{22}NCl$, 347.1441; found, 347.1437.

*1-(4-Chlorophenyl)-1-cyclopropyl-4,9-dimethyl-4,9-dihydro-1H-carbazole (**3g**).* Colorless oil; yield = 11% (19 mg) (method A), 28% (49 mg) (method B); isolated as a ∼1/1.7 mixture of diastereoisomers; R_f = 0.21 (hexane/diethyl ether, 200/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.04−0.13 (m, 1H, maj), 0.19−0.26 (m, 1H, min), 0.28−0.37 (m, 1H, maj), 0.38−0.46 (m, 1H, min), 0.73−0.92 (m, 4H, both isomers), 1.47 (d, J = 7.0 Hz, 3H), 1.49 (d, J = 7.1 Hz, 3H), 1.66−1.76 (m, 1H, maj), 1.79−1.86 (m, 1H, min), 3.28 (s, 3H, min), 3.32 (s, 3H, maj), 3.67−3.81 (m, 2H, both isomers), 5.17 (dd, J = 9.9, 1.6 Hz, 1H, min), 5.18 (dd, J = 10.0, 2.1 Hz, 1H, maj), 5.84 (dd, J = 10.0, 3.1 Hz, 1H, maj), 5.90 (dd, J = 9.9, 3.9 Hz, 1H, min), 7.06−7.13 (m, 2H, both isomers), 7.14−7.21 (m, 2H, both isomers), 7.23−7.44 (m, 10H, both isomers), 7.61−7.67 (m, 2H, both isomers). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ −0.4 (CH_2, maj), 0.1 (CH_2, min), 1.9 (CH_2, both isomers), 17.3 (CH, min), 17.9 (CH, maj), 21.5 (CH_3, maj), 21.9 (CH_3, min), 28.4 (CH, maj), 28.5 (CH, min), 30.3 (CH_3, min), 30.4 (CH_3, maj), 44.1 (C, maj), 44.2 (C, min), 107.9 (CH, both isomers), 112.0 (C, maj), 112.1 (C, min), 117.78 (CH, maj), 117.83 (CH, min), 117.9 (CH, min), 118.3 (CH, maj), 120.2 (CH, both isomers), 124.7 (C, both isomers), 126.3 (CH, maj), 126.7 (CH, min), 127.58 (2 × CH, min), 127.64 (2 × CH, maj), 128.1 (2 × CH, both isomers), 130.4 (CH, min), 130.7 (CH, maj), 131.0 (C, both isomers), 136.2 (C, maj), 136.3 (C, min), 136.7 (C, min), 136.9 (C, maj), 145.0 (C, maj), 145.1 (C, min). LRMS (70 eV, EI): m/z (%) 349 [$(M + 2)^+$, 27], 348 [$(M + 1)^+$, 19], 347 (M^+, 72), 332 (100). HRMS: calcd for $C_{23}H_{22}NCl$, 347.1441; found, 347.1428.

*4-Isopropyl-1,9-dimethyl-4-phenyl-4,9-dihydro-1H-carbazole (**2h**).* White solid; yield = 76% (120 mg) (method A); the two diastereoisomers (A and B) were isolated separately.

Isomer A. White solid; mp 126−128 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.65 (d, J = 6.7 Hz, 3H), 1.07 (d, J = 6.7 Hz, 3H), 1.47 (d, J = 6.9 Hz, 3H), 3.32 (sept, J = 6.7, 1H), 3.60−3.72 (m, 1H), 3.70 (s, 3H), 5.87 (dd, J = 10.1, 1.7 Hz, 1H), 6.17 (dd, J = 10.1, 3.9 Hz, 1H), 6.89−6.97 (m, 1H), 7.04−7.16 (m, 2H), 7.22−7.34 (m, 3H), 7.55−7.67 (m, 3H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 17.8 (CH_3), 18.7 (CH_3), 22.0 (CH_3), 28.7 (CH), 30.1 (CH_3), 31.9 (CH), 50.7 (C), 108.8 (CH), 113.6 (C), 118.5 (CH), 120.1 (CH), 120.5 (CH), 125.0 (C), 125.5 (CH), 127.9 (2 × CH), 128.2 (2 × CH), 129.2 (CH), 130.6 (CH), 137.5 (C), 137.6 (C), 146.4 (C). LRMS (70 eV, EI): m/z (%) 315 (M^+, 3), 273 (24), 272 (100), 257 (34). HRMS: calcd for $C_{23}H_{25}N$, 315.1987; found, 315.1982.

Isomer B. White solid; mp 153−155 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.81 (d, J = 6.7 Hz, 3H), 1.14 (d, J = 6.7 Hz, 3H), 1.47 (d, J = 6.9 Hz, 3H), 3.32 (sept, J = 6.7, 1H), 3.67−3.78 (m, 1H), 3.72 (s, 3H), 5.76 (dd, J = 10.1, 1.6 Hz, 1H), 6.10 (dd, J = 10.1, 4.1 Hz, 1H), 6.81−6.89 (m, 1H), 7.02−7.15 (m, 2H), 7.22−7.35 (m, 4H), 7.47−7.54 (m, 2H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 18.4 (CH_3), 19.8 (CH_3), 21.7 (CH_3), 28.6 (CH), 30.1 (CH_3), 31.0 (CH), 50.7 (C), 108.6 (CH), 113.2 (C), 118.3 (CH), 120.1 (CH), 120.5 (CH), 125.1 (C), 125.4 (CH), 127.7 (2 × CH), 128.5 (2 × CH), 129.5 (CH), 130.4 (CH), 137.4 (C), 137.6 (C), 146.3 (C). LRMS (70 eV, EI): m/z (%) 315 (M^+, 5), 273 (33), 272 (100), 257 (50). HRMS: calcd for $C_{23}H_{25}N$, 315.1987; found, 315.1988.

*1-Isopropyl-4,9-dimethyl-1-phenyl-4,9-dihydro-1H-carbazole (**3h**).* White solid; yield = 8% (13 mg) (method A); isolated as a ∼1/10 mixture of diastereoisomers, and only the data for the major diastereoisomer are reported; mp 120−122 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.56 (d, J = 6.7 Hz, 3H), 1.22 (d, J = 6.7 Hz, 3H), 1.60 (d, J = 7.1 Hz, 3H), 3.10 (sept, J = 6.7, 1H), 3.27 (s, 3H), 3.72−3.81 (m, 1H), 5.61 (dd, J = 10.1, 2.2 Hz, 1H), 6.05 (dd, J = 10.1, 3.1 Hz, 1H), 7.02−7.08 (m, 1H), 7.09−7.14 (m, 1H), 7.15−7.22 (m, 2H), 7.26−7.34 (m, 2H), 7.42−7.50 (m, 2H), 7.61−7.67 (m, 1H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 18.69 (CH_3), 18.74 (CH_3), 22.6 (CH_3), 29.5 (CH), 30.9 (CH_3), 31.7 (CH), 49.3 (C), 108.7 (CH), 113.0 (C), 118.6 (CH), 119.1

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(CH), 120.8 (CH), 125.6 (C), 126.1 (CH), 127.8 (CH), 128.1 (2 × CH), 129.2 (2 × CH), 131.4 (CH), 137.5 (C), 138.0 (C), 144.4 (C). LRMS (70 eV, EI): *m*/*z* (%) 315 (M^+, 10), 273 (23), 272 (100), 257 (30). HRMS: calcd for $C_{23}H_{25}N$, 315.1987; found, 315.1985.

*4-Cyclopropyl-1-isopropyl-9-methyl-4-phenyl-4,9-dihydro-1H-carbazole (**2i**).* Colorless oil; yield = 70% (119 mg) (method A); isolated as a ∼1/1.2 mixture of diastereoisomers; R_f = 0.20 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.00−0.11 (m, 1H), 0.11−0.22 (m, 1H), 0.41−0.67 (m, 2H), 0.60 (d, *J* = 6.9 Hz, 3H), 0.67−0.86 (m, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.85−0.95 (m, 1H), 1.19 (d, *J* = 7.0 Hz, 3H, min), 0.60 (d, *J* = 6.9 Hz, 3H, maj), 1.80−1.90 (m, 1H, min), 1.93−2.05 (m, 1H, maj), 2.39−2.54 (m, 2H), 3.57−3.63 (m, 1H), 3.67−3.71 (m, 1H), 3.75 (s, 3H, maj), 3.76 (s, 3H, min), 5.58 (dd, *J* = 10.2, 1.7 Hz, 1H, maj), 5.66 (dd, *J* = 10.3, 2.0 Hz, 1H, min), 5.87 (dd, *J* = 10.3, 3.5 Hz, 1H, min), 5.92 (dd, *J* = 10.2, 3.8 Hz, 1H, maj), 6.79−6.86 (m, 1H), 6.86−6.92 (m, 1H), 7.03−7.16 (m, 5H), 7.16−7.36 (m, 7H), 7.49−7.55 (m, 2H), 7.58−7.63 (m, 2H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 0.9 (CH_2), 2.5 (CH_2), 2.6 (CH_2), 3.3 (CH_2), 17.1 (CH_3), 18.0 (CH_3), 19.4 (CH), 20.7 (CH_3), 20.9 (CH_3), 21.9 (CH), 30.9 (CH_3, both isomers), 31.5 (CH, both isomers), 39.4 (CH), 40.0 (CH), 45.9 (C), 46.2 (C), 108.9 (CH, both isomers), 114.8 (C), 115.1 (C), 118.5 (CH), 118.6 (CH), 119.9 (CH), 120.4 (CH), 120.7 (CH, both isomers), 122.7 (CH), 123.0 (CH), 125.6 (C, both isomers), 125.7 (CH), 125.9 (CH), 127.8 (2 × CH), 127.95 (2 × CH), 127.97 (2 × CH), 128.02 (2 × CH), 132.7 (CH), 133.4 (CH), 136.3 (C), 136.5 (C), 138.1 (C), 138.2 (C), 148.4 (C), 149.0 (C). LRMS (70 eV, EI): *m*/*z* (%) 341 (M^+, 21), 298 (100), 257 (47). HRMS: calcd for $C_{25}H_{27}N$, 341.2144; found, 341.2145.

*1-Cyclopropyl-4-isopropyl-9-methyl-1-phenyl-4,9-dihydro-1H-carbazole (**3i**).* White solid; yield = 72% (123 mg) (method B); isolated as a ∼1/1.4 mixture of diastereoisomers; R_f = 0.32 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −0.04 to 0.05 (m, 1H), 0.22−0.32 (m, 1H), 0.39−0.47 (m, 2H), 0.62 (d, *J* = 6.8 Hz, 3H, maj), 0.70 (d, *J* = 6.8 Hz, 3H, min), 0.73−0.90 (m, 4H), 1.21 (d, *J* = 7.0 Hz, 3H, maj), 1.25 (d, *J* = 7.0 Hz, 3H, min), 1.64−1.79 (m, 1H, maj), 1.78−1.87 (m, 1H, min), 2.68−1.89 (m, 2H, both isomers), 3.33 (s, 3H, maj), 3.34 (s, 3H, min), 3.69−3.74 (m, 1H, maj), 3.77−3.80 (m, 1H, min), 5.36 (dd, *J* = 10.2, 2.3 Hz, 1H, maj), 5.38 (dd, *J* = 10.2, 1.9 Hz, 1H, min), 5.86−5.93 (m, 2H, both isomers), 7.04−7.12 (m, 2H), 7.13−7.37 (m, 12H), 7.48−7.55 (m, 2H), 7.65−7.72 (m, 2H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 0.3 (CH_2, maj), 1.3 (CH_2, min), 2.8 (CH_2, min), 3.2 (CH_2, maj), 17.0 (CH_3, maj), 17.8 (CH_3, min), 18.8 (CH, min), 19.7 (CH, maj), 20.7 (CH_3, maj), 21.1 (CH_3, min), 30.7 (CH, maj), 30.9 (CH, min), 31.3 (CH_3, min), 31.5 (CH_3, maj), 40.6 (CH, maj), 41.2 (CH, min), 45.4 (C, min), 45.5 (C, maj), 108.8 (CH, min), 108.9 (CH, maj), 111.1 (C, maj), 111.2 (C, min), 118.5 (CH, maj), 118.6 (CH, min), 119.3 (CH, min), 119.4 (CH, maj), 120.9 (CH, maj), 121.0 (CH, min), 124.8 (CH, min), 125.0 (CH, maj), 125.77 (C, maj), 125.84 (C, min), 126.3 (CH, min), 126.4 (CH, maj), 127.4 (2 × CH, min), 127.5 (2 × CH, maj), 128.5 (2 × CH, min), 128.6 (2 × CH, maj), 130.6 (CH, maj), 130.9 (CH, min), 137.8 (C, min), 137.9 (C, maj), 139.0 (C, maj), 139.2 (C, min), 147.5 (C, min), 147.6 (C, maj). LRMS (70 eV, EI): *m*/*z* (%) 341 (M^+, 4), 298 (100), 257 (48). HRMS: calcd for $C_{25}H_{27}N$, 341.2144; found, 341.2145.

*4-Cyclopropyl-9-methyl-1,4-diphenyl-4,9-dihydro-1H-carbazole (**2j**).* Yellow solid; yield = 82% (154 mg) (method A); isolated as a ∼1/1.3 mixture of diastereoisomers; R_f = 0.23 (hexane/AcOEt, 20/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.22−0.40 (m, 3H), 0.42−0.52 (m, 1H), 0.59−0.70 (m, 2H), 0.71−0.95 (m, 2H), 1.92−2.01 (m, 1H), 2.02−2.12 (m, 1H), 3.32 (s, 3H, maj), 3.36 (s, 3H, min), 4.80−4.84 (m, 1H, maj), 4.92 (dd, *J* = 4.0, 1.9 Hz, 1H, min), 5.40 (dd, *J* = 9.9, 1.9 Hz, 1H, min), 5.47 (dd, *J* = 9.9, 2.3 Hz, 1H, maj), 5.83 (dd, *J* = 9.9, 3.4 Hz, 1H, maj), 5.92 (dd, *J* = 9.9, 4.0 Hz, 1H, min), 6.84−6.92 (m, 2H), 7.07−7.14 (m, 2H), 7.15−7.40 (m, 20H, both isomers), 7.59−7.64 (m, 2H), 7.70−7.75 (m, 2H).^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.4 (CH_2, maj), 2.1 (CH_2, min), 2.90 (CH_2, min), 2.92 (CH_2, maj), 20.0 (CH, min), 20.9 (CH, maj), 30.1 (CH_3, min), 30.4 (CH_3, maj), 41.1 (CH, both isomers), 45.90 (C, maj), 45.94 (C, min), 108.9 (CH, both isomers), 115.0 (C, maj), 116.1 (C, min), 118.6 (CH, both isomers), 120.1 (CH, min), 120.3 (CH, maj), 121.0 (CH, both isomers), 125.1 (C, min), 125.2 (C, maj), 125.9 (CH, min), 126.1 (CH, maj), 126.8 (CH, min), 126.9 (CH, maj), 127.9 (CH, min), 127.96 (CH, maj), 127.97 (4 × CH), 128.02 (4 × CH), 128.1 (2 × CH, min), 128.2 (2 × CH, maj), 129.0 (2 × CH, min), 129.1 (2 × CH, maj), 129.4 (CH, maj), 129.5 (CH, min), 134.1 (C, min), 134.8 (C, maj), 137.6 (C, min), 137.7 (C, maj), 143.0 (C, min), 143.2 (C, maj), 148.2 (C, maj), 148.4 (C, min). LRMS (70 eV, EI): isomer 1: *m*/*z* (%) 375 (M^+, 57), 334 (100), 298 (12), 257 (21); isomer 2: *m*/*z* (%) 375 (M^+, 64), 334 (100), 298 (34), 257 (31). HRMS: calcd for $C_{28}H_{25}N$, 375.1987; found, 375.1990.

*9-Methyl-1,4,4-triphenyl-4,9-dihydro-1H-carbazole (**2k**).* White solid; yield = 78% (160 mg) (method A); mp 221−223 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.41 (s, 3H), 4.92 (dd, *J* = 4.0, 1.9 Hz, 1H), 6.00 (dd, *J* = 9.8, 4.0 Hz, 1H), 6.20 (dd, *J* = 9.8, 1.9 Hz, 1H), 6.83−6.92 (m, 1H), 7.06−7.41 (m, 16H), 7.46−7.52 (m, 2H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 30.1 (CH_3), 41.1 (CH), 52.4 (C), 108.9 (CH), 113.9 (C), 118.8 (CH), 120.8 (CH), 121.2 (CH), 125.6 (CH), 125.8 (C), 126.1 (CH), 126.3 (CH), 126.9 (CH), 127.8 (2 × CH), 128.06 (2 × CH), 128.07 (2 × CH), 129.0 (2 × CH), 129.1 (2 × CH), 129.2 (2 × CH), 134.6 (CH), 135.2 (C), 137.6 (C), 142.7 (C), 146.0 (C), 147.1 (C). LRMS (70 eV, EI): *m*/*z* (%) 411 (M^+, 56), 334 (100), 319 (14). HRMS: calcd for $C_{31}H_{25}N$, 411.1987; found, 411.1982.

*4-Cyclopropyl-1,9-dimethyl-1,4-diphenyl-4,9-dihydro-1H-carbazole (**2l**).* White solid; yield = 86% (167 mg) (method A); isolated as a ∼1/1.4 mixture of diastereoisomers; R_f = 0.22 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.26−0.34 (m, 1H), 0.34−0.48 (m, 3H), 0.57−0.65 (m, 1H), 0.66−0.73 (m, 1H), 0.73−0.87 (m, 2H), 1.90−1.99 (m, 1H), 1.99 (s, 3H, maj), 2.00 (s, 3H, min), 2.07−2.16 (m, 1H), 3.28 (s, 3H, maj), 3.34 (s, 3H, min), 5.27 (d, *J* = 9.9 Hz, 1H, min), 5.36 (d, *J* = 9.8 Hz, 1H, maj), 5.61 (d, *J* = 9.8 Hz, 1H, maj), 5.62 (d, *J* = 9.9 Hz, 1H, min), 6.84−6.93 (m, 2H), 7.07−7.16 (m, 4H), 7.16−7.40 (m, 18H), 7.61−7.66 (m, 2H), 7.69−7.75 (m, 2H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.7 (CH_2, min), 1.9 (CH_2, maj), 3.00 (CH_2, min), 3.03 (CH_2, maj), 20.1 (CH, min), 20.4 (CH, maj), 27.0 (CH_3, maj), 27.1 (CH_3, min), 31.1 (CH_3, maj), 31.3 (CH_3, min), 41.3 (C, maj), 41.6 (C, min), 45.8 (C, min), 46.0 (C, maj), 108.88 (CH, maj), 108.92 (CH, min), 114.4 (C, maj), 115.5 (C, min), 118.68 (CH, maj), 118.71 (CH, min), 120.2 (CH, min), 120.4 (CH, maj), 121.0 (CH, maj), 121.1 (CH, min), 124.9 (C, min), 125.1 (C, maj), 125.9 (CH, min), 126.0 (CH, min), 126.1 (CH, maj), 126.5 (2 × CH, min), 126.8 (2 × CH, maj), 127.0 (CH, maj), 127.9 (2 × CH, min), 128.05 (2 × CH, maj), 128.09 (2 × CH, min), 128.14 (2 × CH, maj), 128.7 (2 × CH, min), 128.8 (2 × CH, maj), 135.2 (CH, maj), 135.6 (CH, min), 137.8 (C, maj), 138.0 (C, min), 138.4 (C, min), 139.1 (C, maj), 146.23 (C, min), 146.25 (C, maj), 148.3 (C, min), 148.4 (C, maj). LRMS (70 eV, EI): *m*/*z* (%) 389 (M^+, 51), 348 (100). HRMS: calcd for $C_{29}H_{27}N$, 389.2144; found, 389.2132.

*4-Cyclopropyl-9-methyl-1,1,4-triphenyl-4,9-dihydro-1H-carbazole (**2m**).* White solid; yield = 25% (41% conversion) (56 mg) (method A); mp 184−186 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −0.14 to −0.04 (m, 1H), 0.14−0.23 (m, 1H), 0.51−0.59 (m, 1H), 0.63−0.72 (m, 1H), 1.89−1.98 (m, 1H), 3.18 (s, 3H), 5.44 (dd, *J* = 9.8, 0.6 Hz, 1H), 6.07 (dd, *J* = 9.8, 0.6 Hz, 1H), 6.84−6.89 (m, 1H), 7.07−7.15 (m, 2H), 7.19−7.44 (m, 14H), 7.64−7.70 (m, 2H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.4 (CH_2), 3.2 (CH_2), 20.6 (CH), 32.0 (CH_3), 45.7 (C), 51.3 (C), 109.0 (CH), 116.2 (C), 118.8 (CH), 120.6 (CH), 121.3 (CH), 124.9 (C), 126.1 (CH), 126.7 (CH), 126.8 (CH), 127.3 (CH), 128.0 (2 × CH), 128.20 (2 × CH), 128.22 (2 × CH), 128.3 (2 × CH), 129.2 (2 × CH), 129.5 (2 × CH), 134.8 (CH), 137.0 (C), 137.8 (C), 143.6 (C), 144.5 (C), 148.3 (C). LRMS (70 eV, EI): *m*/*z* (%) 451 (M^+, 70), 410 (100), 374 (15), 333 (28). HRMS: calcd for $C_{34}H_{29}N$, 451.2300; found, 451.2300.

*4-Cyclopropyl-9-methyl-4-phenyl-4,9-dihydro-1H-carbazole (**2n**).* Yellow solid; yield = 11% (16 mg) (method B); mp 100−102 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.22−0.30 (m, 1H), 0.31−0.39 (m, 1H), 0.45−0.54 (m, 1H), 0.63−0.72 (m, 1H), 1.83−1.92 (m, 1H), 3.40−3.55 (m, 2H), 3.70 (s, 3H), 5.54 (dt, *J* = 10.0, 2.2 Hz, 1H), 5.97 (dt, *J* = 10.0, 3.5 Hz, 1H), 6.79−6.84 (m, 1H), 6.98−7.03 (m, 1H), 7.04−7.09 (m, 1H), 7.14−7.20 (m, 1H), 7.24−7.31 (m, 3H), 7.54−7.60 (m, 2H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.6 (CH_2), 2.3 (CH_2), 20.1 (CH), 23.6 (CH_2), 29.3 (CH_3), 46.0 (C), 108.7 (CH), 113.2 (C), 118.4 (CH),

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119.7 (CH), 120.5 (CH), 121.2 (CH), 125.6 (C), 125.8 (CH), 127.9 (2 × CH), 128.0 (2 × CH), 132.6 (CH), 133.3 (C), 137.2 (C), 148.7 (C). LRMS (70 eV, EI): *m*/*z* (%) 299 (M^+, 66), 270 (46), 258 (100). HRMS: calcd for $C_{22}H_{21}N$, 299.1674; found, 299.1676.

1-Cyclopropyl-9-methyl-1-phenyl-4,9-dihydro-1H-carbazole (**3n**). White solid; yield = 60% (82 mg) (method B); mp 127−129 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.10−0.21 (m, 1H), 0.31−0.44 (m, 1H), 0.75−0.86 (m, 2H), 1.70−1.81 (m, 1H), 3.30 (s, 3H), 3.40−3.60 (m, 2H), 5.32 (dt, *J* = 10.0, 2.2 Hz, 1H), 6.02 (dt, *J* = 10.0, 3.4 Hz, 1H), 7.08−7.15 (m, 1H), 7.16−7.28 (m, 3H), 7.29−7.37 (m, 2H), 7.41−7.47 (m, 2H), 7.54−7.60 (m, 1H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 0.5 (CH_2), 2.7 (CH_2), 18.9 (CH), 23.4 (CH_2), 31.3 (CH_3), 45.4 (C), 107.3 (C), 108.7 (CH), 118.1 (CH), 118.7 (CH), 121.1 (CH), 124.0 (CH), 126.25 (C), 126.34 (CH), 127.5 (2 × CH), 128.5 (2 × CH), 129.8 (CH), 137.5 (C), 138.4 (C), 147.4 (C). LRMS (70 eV, EI): *m*/*z* (%) 299 (M^+, 100), 258 (85), 243 (23). HRMS: calcd for $C_{22}H_{21}N$, 299.1674; found, 299.1670.

4,9-Dimethyl-4-phenyl-4,9-dihydro-1H-carbazole (**2o**). White solid; yield = 13% (18 mg) (method B); mp 84−86 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.91 (s, 3H), 3.41−3.62 (m, 2H), 3.70 (s, 3H), 5.81 (dt, *J* = 9.9, 2.0 Hz, 1H), 5.90 (dt, *J* = 9.9, 3.3 Hz, 1H), 6.82−6.91 (m, 1H), 7.05−7.18 (m, 3H), 7.22−7.33 (m, 3H), 7.35−7.42 (m, 2H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 23.5 (CH_2), 26.7 (CH_3), 29.3 (CH_3), 42.0 (C), 108.7 (CH), 114.7 (C), 118.3 (CH), 118.4 (CH), 119.4 (CH), 120.5 (CH), 125.3 (C), 125.7 (CH), 127.1 (2 × CH), 128.0 (2 × CH), 132.6 (C), 137.3 (C), 137.9 (CH), 148.3 (C). LRMS (70 eV, EI): *m*/*z* (%) 273 (M^+, 30), 258 (100), 243 (21), 196 (24). HRMS: calcd for $C_{20}H_{19}N$, 273.1517; found, 273.1519.

1,9-Dimethyl-1-phenyl-4,9-dihydro-1H-carbazole (**3o**). White solid; yield = 63% (86 mg) (method B); mp 159−161 °C; R_f = 0.21 (hexane/diethyl ether, 200/1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.90 (s, 3H), 3.27 (s, 3H), 3.46−3.67 (m, 2H), 5.63 (dt, *J* = 9.8, 2.2 Hz, 1H), 5.93 (dt, *J* = 9.8, 3.4 Hz, 1H), 7.08−7.36 (m, 8H), 7.55−7.60 (m, 1H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 23.4 (CH_2), 25.9 (CH_3), 31.0 (CH_3), 41.5 (C), 106.9 (C), 108.6 (CH), 118.2 (CH), 118.8 (CH), 120.3 (CH), 121.2 (CH), 126.2 (CH), 126.4 (C), 126.9 (2 × CH), 128.5 (2 × CH), 136.3 (CH), 137.5 (C), 138.9 (C), 146.6 (C). LRMS (70 eV, EI): *m*/*z* (%) 273 (M^+, 79), 258 (100), 243 (23). HRMS: calcd for $C_{20}H_{19}N$, 273.1517; found, 273.1518.

4-Cyclopropyl-9-methyl-4-(thiophen-2-yl)-4,9-dihydro-1H-carbazole (**2p**). Yellow solid; yield = 20% (31 mg) (method A); mp 132−135 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.25−0.41 (m, 2H), 0.50−0.71 (m, 2H), 1.94−2.05 (m, 1H), 3.35−3.55 (m, 2H), 3.69 (s, 3H), 5.64 (dt, *J* = 10.0, 2.2 Hz, 1H), 5.96 (dt, *J* = 10.0, 3.5 Hz, 1H), 6.88−6.98 (m, 2H), 7.08−7.15 (m, 2H), 7.16−7.19 (m, 1H), 7.20−7.26 (m, 1H), 7.28−7.34 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.8 (CH_2), 2.2 (CH_2), 21.8 (CH), 23.6 (CH_2), 29.3 (CH_3), 43.8 (C), 108.8 (CH), 112.8 (C), 118.6 (CH), 119.9 (CH), 120.6 (CH), 121.4 (CH), 123.8 (CH), 123.9 (CH), 125.7 (C),126.2 (CH), 132.1 (CH), 133.1 (C), 137.2 (C), 154.9 (C). LRMS (70 eV, EI): *m*/*z* (%) 305 (M^+, 85), 277 (21), 264 (100). HRMS: calcd for $C_{20}H_{19}NS$, 305.1238; found, 305.1230.

1-Cyclopropyl-9-methyl-1-(thiophen-2-yl)-4,9-dihydro-1H-carbazole (**3p**). White solid; yield = 40% (61 mg) (method A); mp 124−126 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.19−0.27 (m, 1H), 0.36−0.45 (m, 1H), 0.70−0.83 (m, 2H), 1.82−1.91 (m, 1H), 3.39−3.57 (m, 2H), 3.46 (s, 3H), 5.43 (dt, *J* = 9.9, 2.2 Hz, 1H), 6.04 (dt, *J* = 9.9, 3.4 Hz, 1H), 6.97−7.04 (m, 2H), 7.09−7.16 (m, 1H), 7.19−7.27 (m, 2H), 7.28−7.32 (m, 1H), 7.55−7.59 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.3 (CH_2), 2.4 (CH_2), 20.5 (CH), 23.4 (CH_2), 31.3 (CH_3), 43.0 (C), 107.1 (C), 108.8 (CH), 118.4 (CH), 118.9 (CH), 121.5 (CH), 124.1 (CH), 124.2 (CH), 124.6 (CH), 126.1 (C), 126.7 (CH), 129.6 (CH), 137.5 (C), 137.7 (C), 153.1 (C). LRMS (70 eV, EI): *m*/*z* (%) 305 (M^+, 74), 277 (47), 264 (100). HRMS: calcd for $C_{20}H_{19}NS$, 305.1238; found, 305.1239.

9-Methyl-4,4-diphenyl-4,9-dihydro-1H-carbazole (**2q**). Yellow solid; yield = 24% (40 mg) (method B); mp 205−207 °C. The obtained compound was slightly contaminated with indene **15**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.52 (dd, *J* = 3.5, 2.2 Hz, 2H), 3.71 (s, 3H), 6.06 (dt, *J* = 9.9, 3.5 Hz, 1H), 6.22 (dt, *J* = 9.9, 2.2 Hz, 1H), 6.78−6.86 (m, 1H), 7.04−7.11 (m, 2H), 7.14−7.21 (m, 2H), 7.22−7.37 (m, 9H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 23.5 (CH_2), 29.3 (CH_3), 52.4 (C), 108.7 (CH), 112.3 (C), 118.6 (CH), 119.5 (CH), 120.3 (CH), 120.7 (CH), 126.0 (2 × CH), 127.8 (4 × CH), 129.0 (4 × CH), 133.4 (C), 136.9 (CH), 137.3 (C), 146.7 (2 × C); one quaternary carbon was not observed. LRMS (70 eV, EI): *m*/*z* (%) 335 (M^+, 51), 258 (100), 243 (23), 144 (19). HRMS: calcd for $C_{25}H_{21}N$, 335.1674; found, 335.1674.

9-Methyl-1,1-diphenyl-4,9-dihydro-1H-carbazole (**3q**). White solid; yield = 37% (62 mg) (method B); mp 213−215 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.16 (s, 3H), 3.60 (dd, *J* = 2.8, 1.5 Hz, 1H), 6.05 (dt, *J* = 9.8, 2.8 Hz, 1H), 6.09 (dt, *J* = 9.8, 1.5 Hz, 1H), 7.11−7.16 (m, 1H), 7.17−7.30 (m, 4H), 7.31−7.36 (m, 8H), 7.60−7.64 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 23.3 (CH_2), 31.7 (CH_3), 51.8 (C), 108.1 (C), 108.8 (CH), 118.4 (CH), 118.9 (CH), 120.9 (CH), 121.5 (CH), 126.3 (C), 126.5 (2 × CH), 128.2 (4 × CH), 129.2 (4 × CH), 135.9 (CH), 136.8 (C), 137.5 (C), 144.3 (2 × C). LRMS (70 eV, EI): *m*/*z* (%) 335 (M^+, 100), 258 (69), 243 (23). HRMS: calcd for $C_{25}H_{21}N$, 335.1674; found, 335.1674.

1-Methyl-3-((3-phenyl-1H-inden-1-yl)methyl)-1H-indole (**15**). Brown oil; yield = 13% (22 mg) (method B); R_f = 0.25 (hexane/diethyl ether, 2/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.89 (ddd, *J* = 14.4, 9.5, 0.7 Hz, 1H), 3.43 (ddd, *J* = 14.3, 6.2, 0.7 Hz, 1H), 3.77 (s, 3H), 3.93−4.00 (m, 1H), 6.58 (d, *J* = 2.1 Hz, 1H), 6.95 (bs, 1H), 7.09−7.15 (m, 1H), 7.21−7.29 (m, 2H), 7.29−7.39 (m, 3H), 7.41−7.47 (m, 2H), 7.47−7.51 (m, 1H), 7.54−7.61 (m, 3H), 7.66−7.71 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 27.6 (CH_2), 32.6 (CH_3), 50.4 (CH), 109.3 (CH), 113.0 (C), 118.7 (CH), 119.0 (CH), 120.3 (CH), 121.5 (CH), 123.6 (CH), 125.0 (CH), 126.5 (CH), 127.2 (CH), 127.6 (CH), 127.7 (2 × CH), 128.2 (C), 128.6 (2 × CH), 136.1 (C), 136.9 (CH), 137.2 (C), 143.4 (C), 143.6 (C), 148.8 (C). LRMS (70 eV, EI): *m*/*z* (%) 335 (M^+, 4), 144 (100). HRMS: calcd for $C_{25}H_{21}N$, 335.1674; found, 335.1680.

4,4-Dicyclopropyl-9-methyl-4,9-dihydro-1H-carbazole (**2r**). White foam; yield = 22% (29 mg) (method B); R_f = 0.15 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.18−0.30 (m, 4H), 0.40−0.49 (m, 2H), 0.50−0.58 (m, 2H), 1.30−1.40 (m, 2H), 3.33 (dd, *J* = 3.4, 2.2 Hz, 2H), 3.63 (s, 3H), 5.50 (dt, *J* = 10.2, 2.2 Hz, 1H), 5.92 (dt, *J* = 10.2, 3.4 Hz, 1H), 7.01−7.06 (m, 1H), 7.10−7.16 (m, 1H), 7.27−7.32 (m, 1H), 7.83−7.89 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 0.9 (2 × CH_2), 1.7 (2 × CH_2), 19.9 (2 × CH), 23.8 (CH_2), 29.2 (CH_3), 40.3 (C), 108.7 (CH), 113.4 (C), 118.4 (CH), 120.2 (CH), 120.8 (CH), 122.0 (CH), 126.2 (C), 131.0 (CH), 133.0 (C), 137.1 (C). LRMS (70 eV, EI): *m*/*z* (%) 263 (M^+, 46), 222 (100), 181 (46). HRMS: calcd for $C_{19}H_{21}N$, 263.1674; found, 263.1674.

1,1-Dicyclopropyl-9-methyl-4,9-dihydro-1H-carbazole (**3r**). Colorless oil; yield = 49% (64 mg) (method B); R_f = 0.23 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.14−0.24 (m, 2H), 0.32−0.42 (m, 2H), 0.50−0.60 (m, 2H), 0.61−0.68 (m, 2H), 1.19−1.28 (m, 2H), 3.33 (dd, *J* = 3.3, 2.2 Hz, 2H), 3.99 (s, 3H), 5.40 (dt, *J* = 10.1, 2.2 Hz, 1H), 6.03 (dt, *J* = 10.1, 3.3 Hz, 1H), 7.03−7.09 (m, 1H), 7.15−7.21 (m, 1H), 7.29−7.34 (m, 1H), 7.43−7.47 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 1.2 (2 × CH_2), 3.0 (2 × CH_2), 18.9 (2 × CH), 23.5 (CH_2), 32.3 (CH_3), 39.1 (C), 106.6 (C), 108.6 (CH), 118.0 (CH), 118.6 (CH), 120.9 (CH), 124.8 (CH), 126.3 (C), 129.2 (CH), 137.6 (C), 139.3 (C). LRMS (70 eV, EI): *m*/*z* (%) 263 (M^+, 57), 222 (100), 181 (49). HRMS: calcd for $C_{19}H_{21}N$, 263.1674; found, 263.1678.

4-(4-Chlorophenyl)-9-methyl-1-propyl-4,9-dihydro-1H-carbazole (**2s**). Yellow oil; yield = 75% (126 mg) (method A); isolated as a ∼1/1.4 mixture of diastereoisomers; R_f = 0.22 (hexane/diethyl ether, 100/1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.93 (t, *J* = 7.3 Hz, 3H, maj), 1.01 (t, 7.3 Hz, 3H, min), 1.09−1.26 (m, 1H), 1.29−1.57 (m, 3H), 1.72−2.05 (m, 4H), 3.65−3.86 (m, 2H, both isomers), 3.77 (s, 6H, both isomers), 4.77−4.82 (m, 1H, maj), 4.84−4.89 (m, 1H, min), 5.88−6.02 (m, 4H, both isomers), 6.84−6.99 (m, 3H), 7.07−7.36 (m, 13H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.06 (CH_3, maj), 14.06 (CH_3, min), 18.3 (CH_2, maj), 19.6 (CH_2, min), 30.1 (CH_3, min), 30.2 (CH_3, maj), 33.3 (CH, maj), 33.5 (CH, min), 37.5 (CH_2, maj), 38.7 (CH_2, min), 41.5 (CH, min), 41.6 (CH, maj), 108.8 (CH, both isomers), 109.0 (C, min), 109.9 (C, maj), 118.5 (CH, min), 118.7 (CH, maj), 118.9 (CH, min), 119.0 (CH, maj), 120.8 (CH, maj), 121.0 (CH, min), 125.9 (C, maj), 126.1 (C, min), 126.8 (CH, maj), 127.0 (CH, min), 128.46 (2 × CH,

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maj), 128.54 (2 × CH, min), 129.6 (2 × CH, min), 129.9 (2 × CH, maj), 129.9 (CH, min), 130.6 (CH, maj), 131.71 (C, min), 131.74 (C, maj), 136.9 (C), 137.5 (C), 137.6 (C, min), 137.7 (C), 143.4 (C, min), 144.0 (C, maj). LRMS (70 eV, EI): isomer 1: *m*/*z* (%) 335 (M^+, 37), 292 (100), 257 (66); isomer 2: *m*/*z* (%) 335 (M^+, 50), 304 (100). HRMS: calcd for $C_{22}H_{22}NCl$, 335.1441; found, 335.1435.

*4-(4-Chlorophenyl)-9-methyl-4,9-dihydro-1H-carbazole (**2t**).* White solid; yield = 75% (110 mg) (method A); mp 150−152 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ 3.43−3.62 (m, 2H), 3.70 (s, 3H), 4.81−4.90 (m, 1H), 5.95 (ddt, *J* = 9.9, 3.2, 1.7 Hz, 1H), 6.01 (dtd, *J* = 9.9, 3.2, 1.7 Hz, 1H), 6.87−6.93 (m, 1H), 7.03−7.08 (m, 1H), 7.09−7.16 (m, 1H), 7.19−7.23 (m, 2H), 7.24−7.27 (m, 2H), 7.28−7.32 (m, 1H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 23.6 (CH_2), 29.3 (CH_3), 41.3 (CH), 108.7 (CH), 109.0 (C), 118.0 (CH), 118.6 (CH), 120.8 (CH), 121.3 (CH), 126.1 (C), 128.5 (2 × CH), 129.6 (2 × CH), 130.6 (CH), 131.7 (C), 133.5 (C), 137.2 (C), 144.0 (C). LRMS (70 eV, EI): *m*/*z* (%) 293 (M^+, 100), 182 (59), 167 (27). HRMS: calcd for $C_{19}H_{16}NCl$, 293.0971; found, 293.0975.

*9-Methyl-4-(naphthalen-1-yl)-4,9-dihydro-1H-carbazole (**2u**).* Yellow solid; yield = 74% (114 mg) (method B); R_f = 0.32 (hexane/AcOEtr, 8/1). ^1H NMR (300 MHz, $CDCl_3$): δ 3.44−3.70 (m, 2H), 3.74 (s, 3H), 5.02−5.12 (m, 1H), 5.95−6.12 (m, 2H), 6.82−6.92 (m, 1H), 7.09−7.18 (m, 2H), 7.25−7.38 (m, 2H), 7.38−7.51 (m, 2H), 7.70−7.88 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 23.6 (CH_2), 29.2 (CH_3), 42.1 (CH), 108.4 (CH), 109.3 (C), 118.7 (CH), 118.9 (CH), 120.7 (2 × CH), 125.1 (CH), 125.7 (CH), 126.15 (CH), 126.19 (C), 126.7 (CH), 127.55 (CH), 127.62 (CH), 128.1 (CH), 131.2 (CH), 132.3 (C), 133.1 (C), 133.5 (C), 137.0 (C), 142.3 (C). HRMS: calcd for $C_{23}H_{19}N$, 309.1517; found, 309.1519.

*9-Methyl-1-phenyl-4,9-dihydro-1H-carbazole (**2v**).* White solid; yield = 84% (109 mg) (method A); mp 129−131 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ 3.35 (s, 3H), 3.50−3.69 (m, 2H), 4.80 (tdd, *J* = 5.9, 4.0, 1.7 Hz, 1H), 5.94 (ddt, *J* = 9.8, 4.0, 2.1 Hz, 1H), 6.05 (dtd, *J* = 9.8, 3.3, 1.7 Hz, 1H), 7.09−7.28 (m, 6H), 7.28−7.34 (m, 2H), 7.58 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 23.6 (CH_2), 29.8 (CH_3), 41.2 (CH), 107.4 (C), 108.7 (CH), 118.2 (CH), 118.7 (CH), 121.1 (CH), 123.5 (CH), 126.4 (C), 126.6 (CH), 128.0 (2 × CH), 128.80 (CH), 128.82 (2 × CH), 134.9 (C), 137.2 (C), 143.6 (C). LRMS (70 eV, EI): *m*/*z* (%) 259 (M^+, 100), 258 (40), 182 (44), 167 (29). HRMS: calcd for $C_{19}H_{17}N$, 259.1361; found, 259.1358.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra of all products, selected NOESY spectra, and a CIF for compound **2u**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(57) The formation of species **7** could be supported by our previous theoretical and experimental studies on related reactions of 3-propargylindoles (refs 45−48), whereas the role of spirocyclic complexes **8** as intermediates is well-documented (see, for instance, refs 23, 32, and 33).