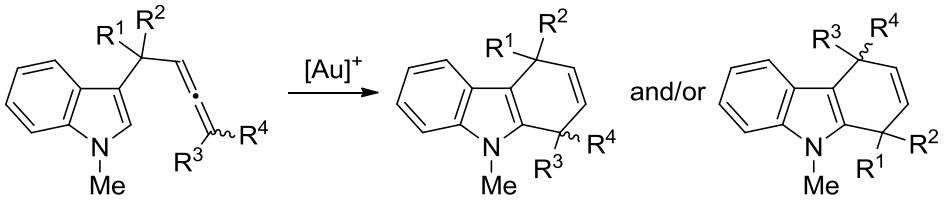
Regioselective Synthesis of Elusive 4,9-Dihydro-1*H*-Carbazoles by Gold-Catalyzed Cycloisomerization of 3-Allenylmethylindoles

*Estela Álvarez, Patricia García-García, Manuel A. Fernández-Rodríguez, and Roberto Sanz**

Departamento de Química, Área de Química Orgánica, Facultad de Ciencias, Universidad de Burgos, Pza. Misael Bañuelos s/n, 09001-Burgos, Spain

rsd@ubu.es

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)



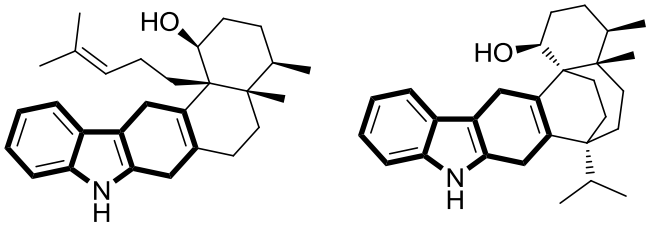
Abstract. A general and efficient synthesis of 4,9-dihydro-1*H*-carbazoles from 3-allenylmethylindoles is reported. The process, catalyzed by a cationic gold(I) complex, involves a formal C2–H bond activation of the indole unit by reaction with allenes. The nature of the substituents at the allylic as well as the terminal position 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 multi-pathway mechanism consistent with all the results described.

Introduction

The carbazole unit is a key heterocyclic structure 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-B (Figure 1).[14] The scarce 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, and ring-closing methathesis.[19]

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



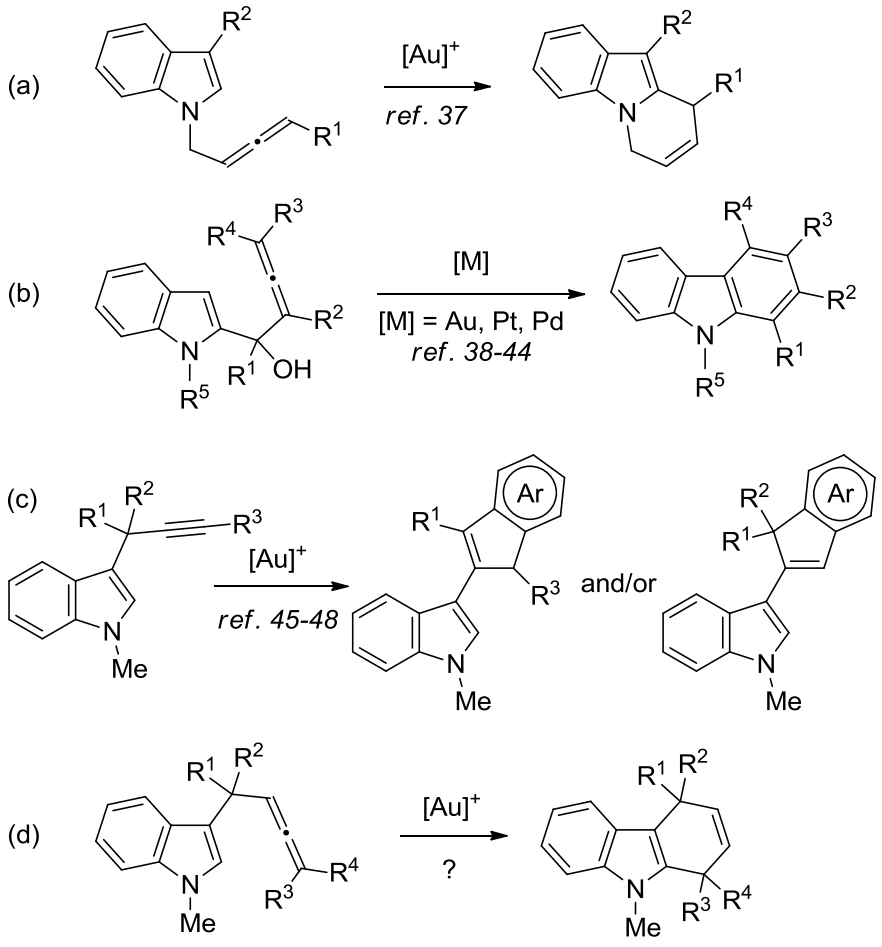
dihydrotubingensins A-B

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 hetero-polycyclic 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 dihydro-pyrido[1,2-a]-1*H*-indoles has been described (Scheme 1a).[37] Moreover, several

cyclizations 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] or Pd[44] (Scheme 1b).

In this context, and taking advantage of our experience in the gold-catalyzed isomerization of 3-propargylindoles that 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).

SCHEME 1. Reported cycloisomerizations of allenylmethyl- and propargylindoles and proposed synthesis of dihydrocarbazoles.



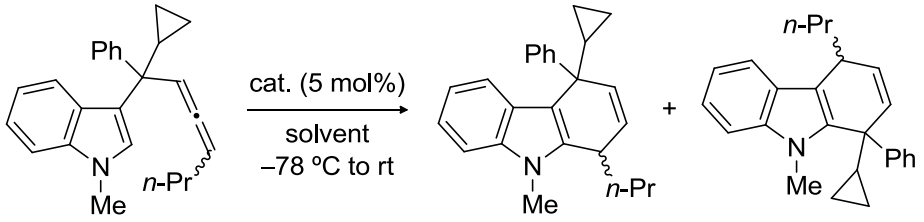
Results and Discussion

To our aim, we initially selected 3-(1-cyclopropyl-1-phenylhepta-2,3-dien-1-yl)-1-methyl-1*H*-indole **1a** (a disubstituted allene derivative) as model substrate. Preliminary essays conducted at rt in the presence of $Ph_3PAuNTf_2$ as catalyst afforded a complex mixture of compounds. Pleasantly, a clean cycloisomerization selectively occurred by setting up the reaction at –78 ºC and allowing the mixture to reach rt, thus affording a 1/2.3 mixture of regioisomers **2a** and **3a** (Table 1, entry 1). On the contrary, no evolution of the allene derivative was observed in reactions on the presence of others 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. Same ratio of regioisomers (1/2.3) was obtained in reactions conducted at –50 ºC or at other temperatures between rt and –78 ºC. No reaction was observed either with Ph_3PAuCl or $AgNTf_2$ (entries 2–3), whereas a messy reaction and a decrease in the selectivity was observed with $XPhosAuNTf_2$ (entry 4). Remarkably, a switch in the regioselectivity occurred using an equimolecular mixture of PPh_3AuCl and $AgNTf_2$ as 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 non innocent presence of the silver salt.[49] This assumption was confirmed with an experiment conducted with the combination PPh_3AuNTf_2/AgCl as catalyst that also switched the regioselectivity to give in this case a 1.2/1 ratio of **2a**/**3a** (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 product ratio **2a**/**3a** could be slightly improved using a triflate anion (entry 10 *vs* entries 11–13). In contrast, the solvent has a crucial effect in the regioselectivity. Thus, reactions catalyzed by $Ph_3PAuNTf_2$ and conducted in CH_2Cl_2, DCE or trifluorotoluene gave **3a** as major isomer while analogous experiments conducted in non-halogenated solvents such as DME, THF, MeOH or toluene switched the selectivity to **2a** (entries 1, 14–15 *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, that we had previously observed that favoured the formation of **2a**, we were able to nearly exclusively obtain dihydrocarbazole **2a** (entry 21).

TABLE 1. Cycloisomerization of 3-allenylmethylindole 1a: Effect of the reaction conditions on the selectivity.



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

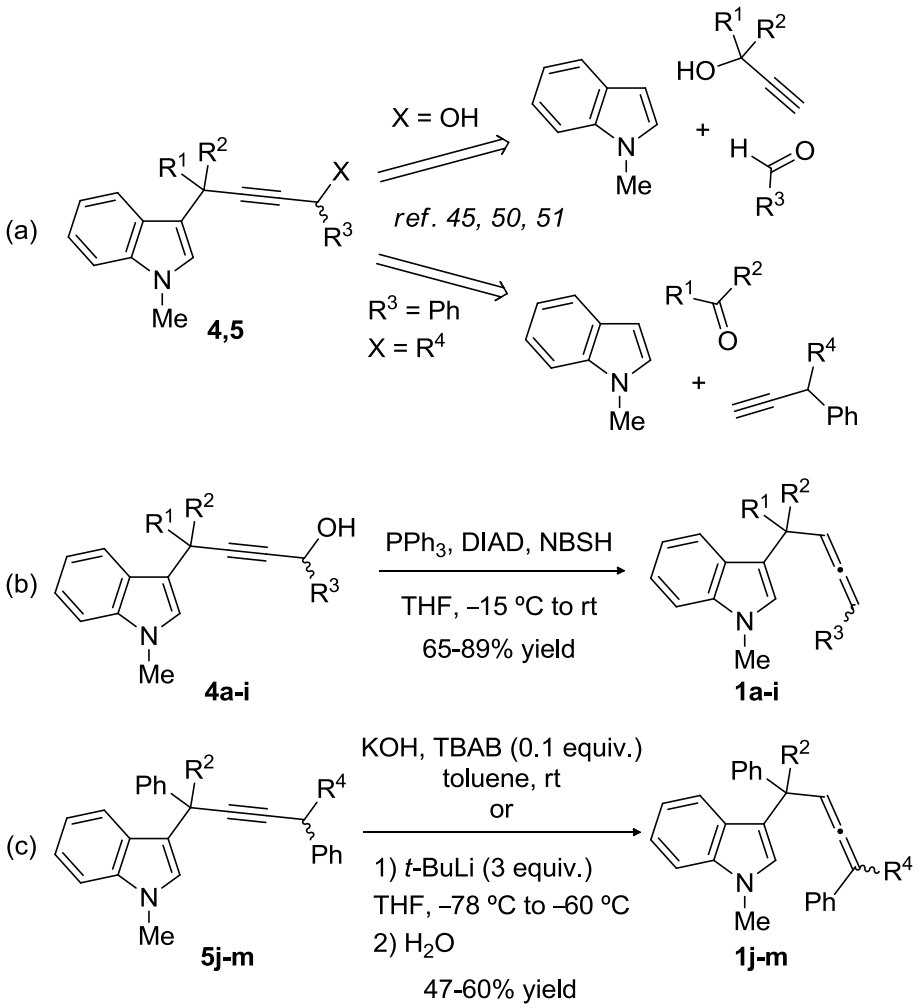
entry	catalyst	solvent	**2a** / **3a** [a]
1	$Ph_3PAuNTf_2$	CH_2Cl_2	1 / 2.3
2	Ph_3PAuCl	CH_2Cl_2	-
3	$AgNTf_2$	CH_2Cl_2	-
4	$XPhosAuNTf_2$	CH_2Cl_2	1 / 1.2 [b]
5	$Ph_3PAuCl/AgNTf_2$	CH_2Cl_2	2 / 1
6	$Ph_3PAuNTf_2/AgCl$	CH_2Cl_2	1.2 / 1
7	$IPrAuCl^c/AgNTf_2$	CH_2Cl_2	2.2 / 1 [b]
8	$(PhO)_3PAuCl/AgNTf_2$	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 ^{1}H NMR 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.

Notably, our studies on reaction conditions show 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 obtaining dihydrocarbazoles **2a** and **3a** selectively, we decided to explore the influence of the starting substrate in 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*-methyl indole, carbonyl and alkyne compounds applying 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 DIAD (diisopropyl azodicarboxylate), followed by the addition of NBSH (*o*-nitrobenzenesulfonylhydrazide),[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).

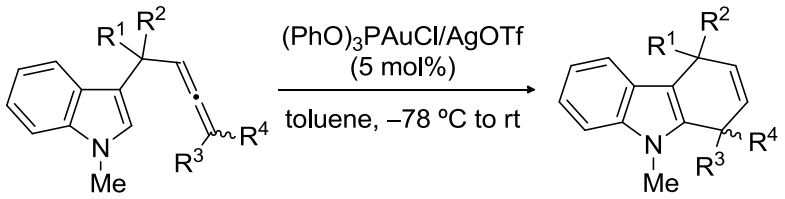
SCHEME 2. Synthesis of allenylmethylindoles 1a-i, j-m.



Having synthesized allenylmethylindoles **1a-m** bearing different substituents (R^1-R^4), their reactions were investigated under both conditions A (Table 2) and B (Table 3). As previously observed for **1a** (Table 2, entry 1), reactions under method A of disubstituted allenes **1b-k** (R^4 = H) (Table 2, entries 2–11) as well as trisubstituted allene derivatives **1l-m** ($R^4 \neq$ H, entries 12–13) bearing aryl, linear- or branched-alkyl groups at both allylic and terminal allene positions essentially or exclusively afforded regioisomer **2**. Therefore, using method A, a series of highly substituted 4,9-dihydro-1*H*-carbazoles **2a-m** were regioselectively obtained in good yields. In all the reactions displayed in Table 2 as well as in the ones described later in this paper (depicted in Table 3 and Schemes 4–5), the major regioisomer was

obtained as a ca. 1/1 mixture of diastereomers and could be easily isolated from the minor regioisomer.[55] Furthermore, the structure of the final products was established by NMR experiments.

TABLE 2. Cycloisomerization of 3-allenylmethylindoles 1a-m using Method A: Regioselective synthesis of 4,9-dihydro-1*H*-carbazoles 2.[a]



1 **2**

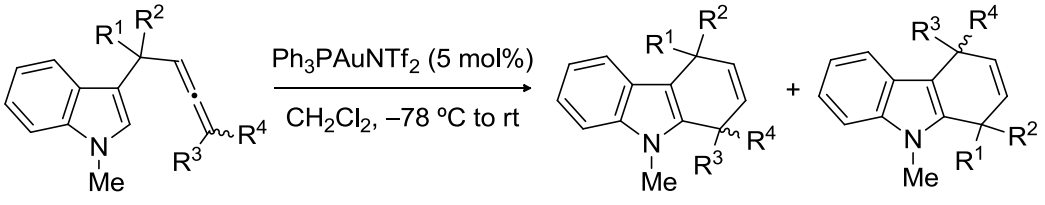
entry	**1**	R^1	R^2	R^3	R^4	**2**	yield (%)[b]
1	**1a**	Ph	*c*-Pr	*n*-Pr	H	**2a**	78
2	**1b**	Ph	Ph	*n*-Pr	H	**2b**	91
3	**1c**	*c*-Pr	*c*-Pr	*n*-Pr	H	**2c**	57
4	**1d**	Me	*c*-Pr	*n*-Pr	H	**2d**	64
5	**1e**	Me	Me	*n*-Pr	H	**2e**	80
6	**1f**	Ph	*c*-Pr	Me	H	**2f**	57[c]
7	**1g**	4-ClC_6H_4	*c*-Pr	Me	H	**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 complete and products **2** were exclusively formed (regioselectivity >20/1) unless otherwise stated. [b] Isolated yield. [c] Ratio **2**/**3**: 3.6/1 (entry 6), 3.8/1 (entry 7), 6.7/1 (entry 8), 5.0/1 (entry 9). [d] 41% conversion.

In contrast, parallel experiments conducted under method B revealed a significant influence of the substitution pattern of the substrate in the selectivity of the cycloisomerization. Thus, whereas the formation of dihydrocarbazole **3a** from the model substrate **1a** was favoured (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 analyzing reactions of substrates **1f,a,i** (with R^3 = Me, *n*-Pr, and *i*-Pr groups, respectively). We can conclude that, under conditions B, the selectivity of the isomerization to dihydrocarbazole **3** could be notably improved by increasing the bulkiness of the alkyl group located at the terminal sp^2 allene carbon atom (Table 3, entries 6 *vs* 1 *vs* 9). On the contrary, isomers **2** appear to be totally favoured for substrates **1j-k** bearing R^3 = Ph (Table 3, entries 10–11). In addition, reactions of trisubstituted allene derivatives **1l-m** (R^3, $R^4 \neq$ H) occurred mostly to decomposition under these conditions (Table 3, entries 12–13). Therefore, among the highly substituted allene derivatives **1a-m** investigated under conditons B only **1a** and **1i** afford useful synthetic yields of the corresponding 4,9-dihydro-1*H*-carbazoles **3a** and **3i** (Table 3, entries 1 and 9) whereas dihydrocarbazoles **3b,f-g** were obtained in modest yields (Table 3, entries 2 and 6–7).

TABLE 3. Effect of the structure of the substrate on the selectivity of the cycloisomerization of 3-allenylmethylindoles 1a-m using Method B.



1 **2** **3**

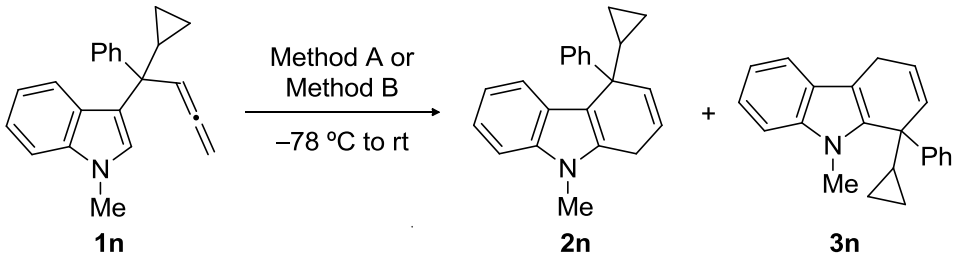
entry	**1**	R^1	R^2	R^3	R^4	**2** / **3** [a]	**3**	yield (%)[b]
1	**1a**	Ph	*c*-Pr	*n*-Pr	H	1/2.3	**3a**	65
2	**1b**	Ph	Ph	*n*-Pr	H	2.1/1	**3b**	20
3	**1c**	*c*-Pr	*c*-Pr	*n*-Pr	H	7.0/1	**3c**	–
4	**1d**	Me	*c*-Pr	*n*-Pr	H	>10/1	**3d**	–
5	**1e**	Me	Me	*n*-Pr	H	>20/1	**3e**	–

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 of the crude mixture. Reactions required 4-6 h and only products **2** and/or **3** were formed unless otherwise stated. [b] Isolated yield. [c] Decomposition was observed.

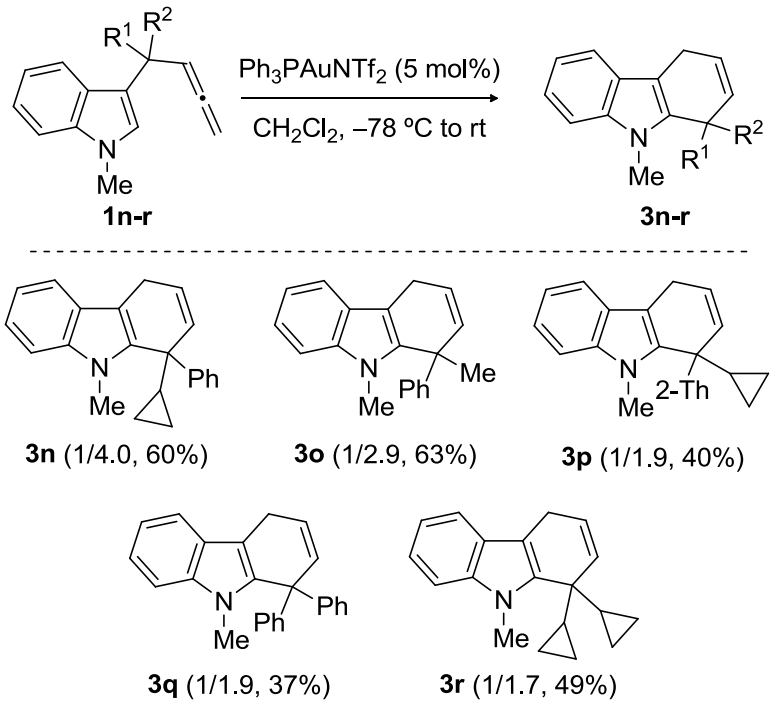
Next, we turned our attention to the isomerization of substrates **1n-r** possessing a terminal allene that were also easily prepared using Myers methodology.[52] Preliminar experiments conducted with allenylmethylindole **1n** gave dyhydrocarbazole **3n** as major regioisomer, in moderate **3**/**2**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

SCHEME 3. Cycloisomerization of allenylmethylindole 1n.



Nevertheless, using 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 in modest ratio, and isolated in moderate to good yields from the corresponding starting allenes **1o-r** (Scheme 4).[55]

SCHEME 4. Synthesis of 4,9-dihydro-1*H*-carbazoles 3n-r from allenylmethylindoles 1n-r bearing a terminal allene moiety.[a]

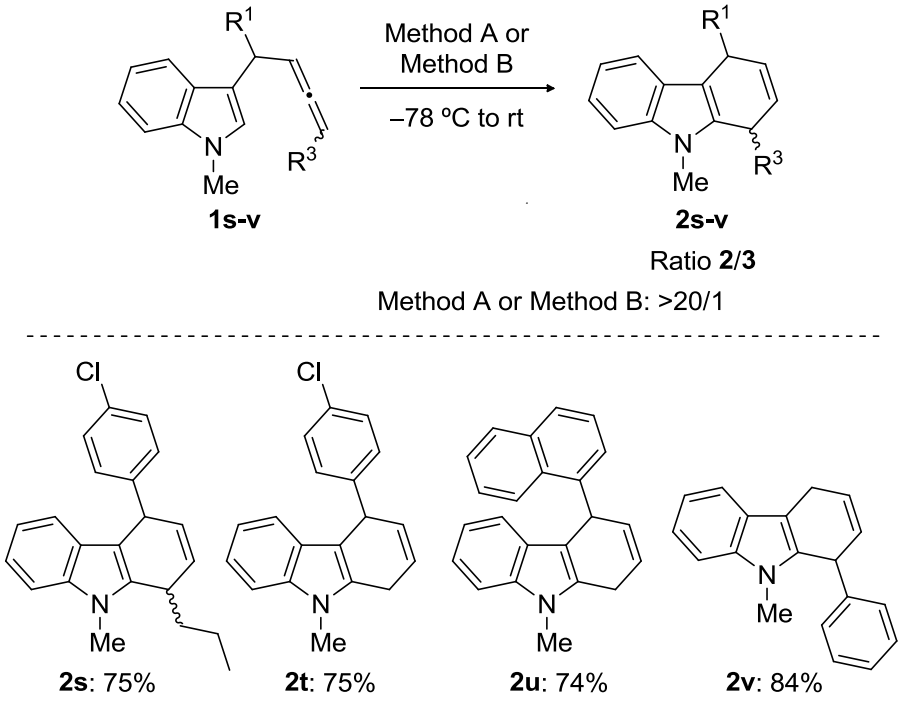


[a] All reactions were conducted under Method B with the exception of substrate **3p** which was prepared using Method A. In brackets regioisomeric ratio **2**/**3** and isolated yield of dihydrocarbazole **3**.

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

afford **3** as major regioisomer in spite of the method used (Scheme 4). On the other hand, the structure of the final products **2s-v** was again established by NMR experiments and confirmed by X-ray diffraction analysis of **2u**.[56]

SCHEME 5. Synthesis of 4,9-dihydro-1*H*-carbazoles 2s-v from allenylmethylindoles 1s-v possessing a tertiary or secondary allylic carbon.[a]



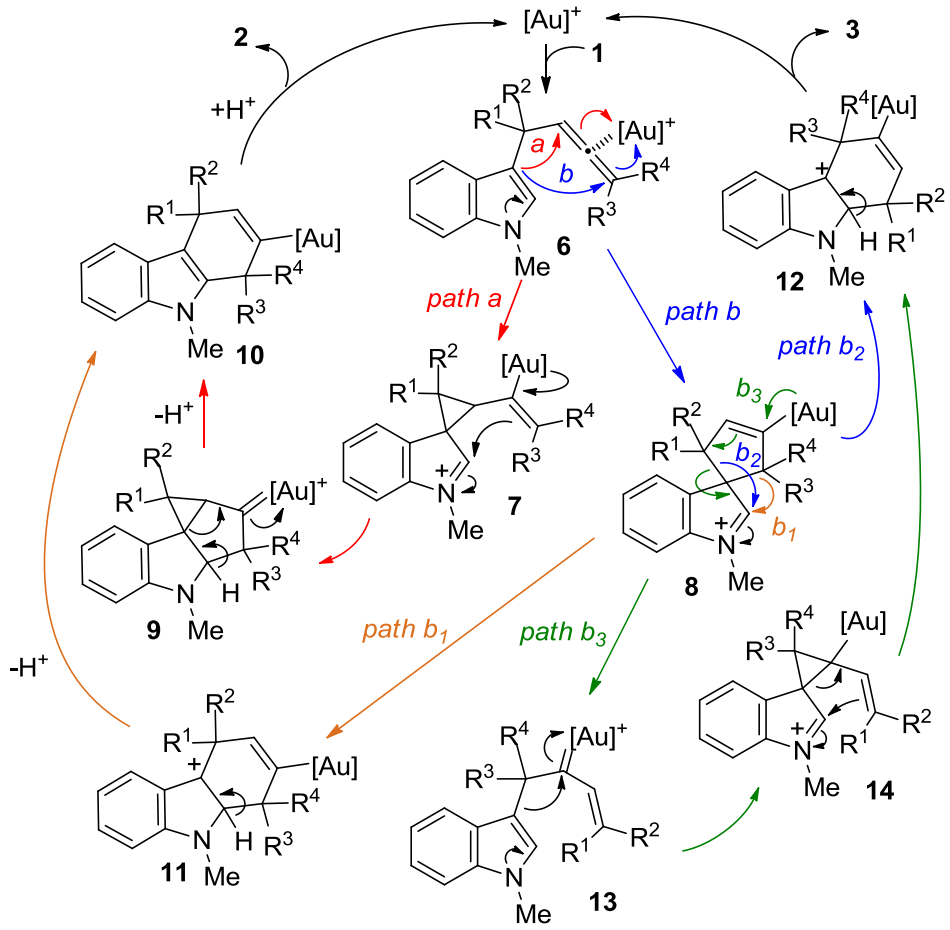
[a] Reactions were conducted under Method A [$(PhO)_3PAuCl$/AgOTf (5 mol%), toluene] with the exception of substrate **2u** which was prepared using Method B [$Ph_3PAuNTf_2$ (5 mol%), CH_2Cl_2].

This comprehensive study revealed that 3-allenylmethylindoles **1** bearing a di- or tri-substituted 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 was favoured using method B provided that the terminal carbon of the allene was 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 includes aryl and linear- or branched-alkyl at both positions. In addition, regioisomeric 4,9-

dihydro-1*H*-carbazoles **3a,i,n-r** were synthesized in moderate to good yields from the corresponding starting substrates **1a,i,n-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 an intramolecular attack of the indole that may occur to both activated carbons 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 sequence of cyclopropane ring opening/protodemetalation to yield dihydrocarbazole **2** through vinyl gold intermediate **10**. On the other hand, at least three different evolutions of intermediate **8** could be possible. One of them, the 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 on cationic gold interemediate species **12** 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 an indole nucleophilic addition on the gold carbenoid giving rise to new spirocyclic derivative **14**, which by a sequence of cyclization/ring opening/protodemetalation 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 the proposed pathways could be operative.

SCHEME 6. Proposed mechanism.

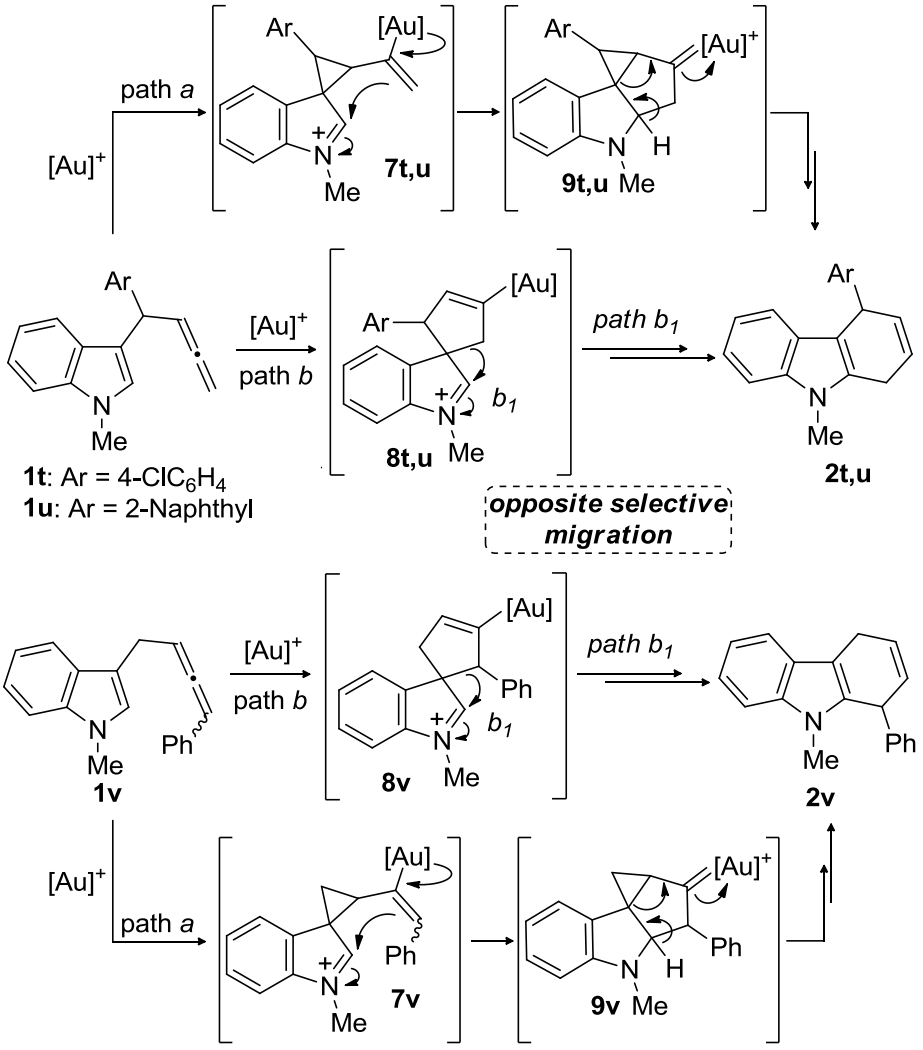


In fact, we have obtained some evidence for the viability of paths *a* and b_3. As illustrated in Scheme 5, reactions of **1t-v** selectively afford products **2t-v** that, based in our proposal, should be formed through *pathway a* and/or b_1 (Schemes 6–7). As shown in Scheme 7, if *path* b_1 would be the only operative route it would imply an opposite selective migration of benzylic *vs* primary alkyl group in the corresponding intermediates **8** (compare intermediates **8t,u** vs **8v**). Therefore, *path a* must be the running mechanism for at least one of this type of substrates. Furthermore, the effect of steric bulk at R^3 using method B conditions, i.e. the improved selectivity to compound **3** by increasing the steric hindrance at R^3 (Me vs *n*-Pr vs *i*-Pr, Table 3, entries 6, 9, and 1, respectively), also account 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

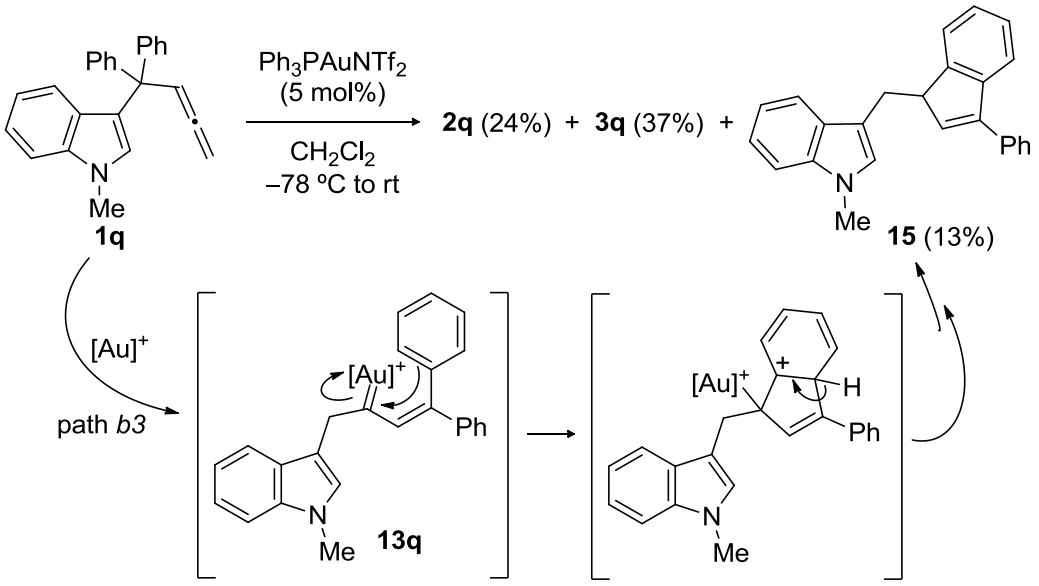
considering that the formation of **7** from **6** should be favoured over the formation of **8** with an increased steric bulk at R^3.

On the other hand, pathway *b₃* is partially working in the case of **1q** as pointed out by the minor formation of indene **15** that 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.

SCHEME 7. Evidence of viability of pathway *a*: Cycloisomerization of allenylmethylindoles 1t-v.



SCHEME 8. Evidence of viability of pathway *b*$_3$: Formation of indene 15 in the reaction of allenylmethylindole 1q.



Conclusions

In conclusion, we have described a gold(I)-catalyzed cyclization of 3-allenylmethylindole derivatives allowing 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 allenes. The synthetic utility of this transformation is ilustrated with the preparation of several new dihydrocarbazoles with a wide variety of substitution patterns in usually good yields. Moreover, a plausible mechanism that involves different pathways has been proposed and some insight into the viability of two of these possible routes has been obtained.

Experimental Section

All reactions involving air sensitive compounds were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated and purged with nitrogen. 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 with F_{254} indicator; the chromatograms were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent and subsequent heating. R_f values are reported on silica gel. 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 ºC for 3 days. NMR spectra were measured on 300 MHz and 400 MHz spectrometers. ^{1}H NMR: 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; m, multiplet; the chemical shifts are reported in ppm using residual solvent peak as reference. ^{13}C NMR spectra were recorded at 75.4 MHz or 100.6 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference and the multiplicities were determined by DEPT experiments. High resolution mass spectra (HRMS) were recorded using EI at 70eV 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 spectra (LRMS) measurements were recorded on an instrument equipped with a HP-5MS column.

Synthesis of allenylmethylindoles 1:

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

vacuum. The resulting crude residue was purified by column chromatography using hexane/Et_2O (40:1) as eluent to obtain the corresponding allenylmethylindoles **1l-m** in the yields reported bellow.

Characterization and spectroscopic data for allenylmethylindoles 1:

3-(1-Cyclopropyl-1-phenylhepta-2,3-dien-1-yl)-1-methyl-1*H*-indole (1a): Colourless 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-1*H*-indole (1b): Colourless 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-1*H*-indole (1c): Colourless 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.

3-(2-Cyclopropylocta-3,4-dien-2-yl)-1-methyl-1*H*-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)- 1*H*-indole (1e): Colourless 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-1*H*-indole (1f): Colourless 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-1*H*-indole (1g): Colourless 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)-1*H*-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-1*H*-indole (1i): Colourless 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-1*H*-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)- 1*H*-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-1*H*-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), 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-1*H*-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-1*H*-indole (1n): Colourless 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)-1*H*-indole (1o): White solid; yield = 52% (142 mg); R_f = 0.18 (hexane/AcOEt, 50:1); ^1H 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-1*H*-indole (1p): White solid; yield = 75% (229 mg); R_f = 0.18 (hexane/diethyl ether, 30:1); ^1H 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-1*H*-indole (1q): Yellow oil; yield = 46% (308 mg); R_f = 0.31 (hexane/diethyl ether, 30:1); ^1H 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-1*H*-indole (1r): White solid; yield = 60% (158 mg); M.p. 56–58 ºC. ^{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-1*H*-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-1*H*-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), 127.1.6 (CH), 127.28 (C), 127.32 (CH), 127.2 (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)-1*H*-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), 129.92 (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 ºC. The corresponding allenylmethylindole **1** (0.5 mmol) in dry toluene (1 mL) was added and the mixture was stirred allowing it to slowly reach rt until complete consumption of starting material (as determined by TLC or GC-MS analysis). After filtration through a short pad of celite, using CH_2Cl_2 as eluent, the solvent was removed under reduced pressure and the crude residue purified by flash chromatography on deactivated silica gel,

using mixtures of hexane/diethyl ether or hexane/AcOEt as 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 yields depicted in Table 2 and Schemes 4–5. The minor regioisomer, if formed in significant amount, was also isolated in the yields reported below. Both dihydrocarbazoles were obtained as a ca. 1/1 mixture 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 ºC. The resulting mixture was stirred allowing it to slowly reach rt until complete consumption of starting material (as determined by TLC or GC-MS analysis). After filtration through a short pad of celite, using CH_2Cl_2 as eluent, the solvent was removed under reduced pressure and the crude residue purified by flash chromatography on deactivated silica gel, using mixtures of hexane/diethyl ether or hexane/AcOEt as 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 yields depicted in Table 3 and Schemes 4–5. The minor regioisomer, if formed in significant amount, was also isolated in the yields reported below. Both dihydrocarbazoles were obtained as a ca. 1/1 mixture 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-1*H*-carbazole (2a): Colourless 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, may), 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-1*H*-carbazole (3a): Colourless 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-1*H*-carbazole (2b): White solid; yield = 91% (171 mg) (Method A); M.p. = 171–173 ºC. ^{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). LRMS (70 eV, EI): *m/z* (%) 377 (M^+, 49), 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-1*H*-carbazole (3b): White solid; yield = 20% (38 mg) (Method B); M.p. = 160–162 ºC. ^{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-1*H*-carbazole (2c): White solid; yield = 57% (87 mg) (Method A); M.p. = 101–103 ºC. ^{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-1*H*-carbazole (2d): Colourless 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-1*H*-carbazole (2e): Colourless 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, 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-1*H*-carbazole (2f): Colourless 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-1*H*-carbazole (3f): Colourless 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-1*H*-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-1*H*-carbazole (3g): Colourless 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-1*H*-carbazole (2h): White solid; yield = 76% (120 mg) (Method A); Both diastereoisomers (A and B) were isolated separately.

Isomer A: White solid; M.p. 126–128 ºC. ^{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). LRMS (70 eV, EI): *m/z* (%) 315 (M^+, 2), 273 (24), 272 (100), 257 (34). HRMS calcd for $C_{23}H_{25}N$, 315.1987; found, 315.1982.

Isomer B: White solid; M.p. 153–155 ºC. ^{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). 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-1*H*-carbazole (3h): White solid; yield = 8% (13 mg) (Method A); isolated as a ~1:10 mixture of diastereoisomers, the data of the major diastereoisomer are reported; M.p. 120–122 ºC. ^{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 (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-1*H*-carbazole (2i): Colourless 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-1*H*-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 = –0.04–0.05 (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-1*H*-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). LRMS (70 eV, EI): *m/z* (%) 375 (M^+, 61), 334 (100), 298 (30). HRMS calcd for $C_{28}H_{25}N$, 375.1987; found, 375.1990.

9-Methyl-1,4,4-triphenyl-4,9-dihydro-1*H*-carbazole (2k): White solid; yield = 78% (160 mg) (Method A); M.p. 221–223 ºC. ^{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-1*H*-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-1*H*-carbazole (2m): White solid; yield = 25% (41% conversion) (56 mg) (Method A); M.p. 184–186 ºC. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = -0.14–-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 (d, *J* = 9.8, 0.6 Hz, 1H), 6.07 (d, *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-1*H*-carbazole (2n): Yellow solid; yield = 11% (16 mg) (Method B); M.p. 100–102 ºC. ^{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), 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-1*H*-carbazole (3n): White solid; yield = 60% (82 mg) (Method B); M.p. 127–129 ºC. ^{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-1*H*-carbazole (2o): White solid; yield = 13% (18 mg) (Method B); M.p. 84–86 ºC. ^{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-1*H*-carbazole (3o): White solid; yield = 63% (86 mg) (Method B); M.p. 159–161 ºC. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = White solid; *R*f 0.21 (hexane/diethyl ether, 200:1). M.p. 159–161 ºC. ^{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-1*H*-carbazole (2p): Yellow solid; yield = 20% (31 mg) (Method A); M.p. 132–135 ºC. ^{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-1*H*-carbazole (3p): White solid; yield = 40% (61 mg) (Method A); M.p. 124–126 ºC. ^{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-1*H*-carbazole (2q): Yellow solid; yield = 24% (40 mg) (Method B); M.p. 205–207 ºC. The compound was obtained 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 is 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-1*H*-carbazole (3q): White solid; yield = 37% (62 mg) (Method B); M.p. 213–215 ºC. ^{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-1*H*-inden-1-yl)methyl)-1*H*-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-1*H*-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-1*H*-carbazole (3r): Colourless 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-1*H*-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, 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-1*H*-carbazole (2t): White solid; yield = 75% (110 mg) (Method A); M.p. 150–152 ºC. ^{1}H 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-1*H*-carbazole (2u): Yellow solid; yield = 74% (114 mg) (Method B); R_f = 0.32 (hexane/AcOEtr, 8:1). ^{1}H 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-1*H*-carbazole (2v): White solid; yield = 84% (109 mg) (Method A); M.p. 129–131 ºC. ^{1}H 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.

Acknowledgment. We are grateful to the MICINN and FEDER (CTQ2010-15358 and CTQ2009-09949/BQU) for financial support. E.A. thanks MEC for a FPU predoctoral fellowship. P.G.-G. and M.A.F.-R. thank MICINN for "Juan de la Cierva" and "Ramón y Cajal" contracts.

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

References.

(1) Schmidt, A. W.; Reddy, K. R.; Knölker, H.-J. *Chem. Rev.* **2012**, *112*, 3193–3328.
(2) Knölker, H.-J.; Reddy, K. R. In *The Alkaloids*; Cordell, G. A., Ed.; Academic Press: Amsterdam, 2008; Vol. 65, p 1.
(3) Lemasson, F. A.; Strunk, T.; Gerstel, P.; Hennrich, F.; Lebedkin, S.; Barner-Kowollik, C.; Wenzel, W.; Kappes, M. M.; Mayor, M. *J. Am. Chem. Soc.* **2011**, *133*, 652–655.
(4) Li, P.-P.; Chen, Y.; Zhu, J.; Feng, M.; Zhuang, X.; Lin, Y.; Zhan, H. *Chem. Eur. J.* **2011**, *17*, 780–785.
(5) Li, J.; Grimsdale, A. C. *Chem. Soc. Rev.* **2010**, *39*, 2399–2410.
(6) Pirovano, V.; Decataldo, L.; Rossi, E.; Vicente, R. *Chem. Commun.* **2013**, *49*, 3594–3596.
(7) Mohamed, Y. A. M.; Inagaki, F.; Takahashi, R.; Mukai, C. *Tetrahedron* **2011**, *67*, 5133–5141.
(8) Fuwa, H.; Sasaki, M. *Chem. Commun.* **2007**, 2876–2878.
(9) Barluenga, J.; Fañanás, F. J.; Sanz, R.; Fernández, Y. *Chem. Eur. J.* **2002**, *8*, 2034–2036.
(10) Hussain, M.; Tengho Toguem, S.-M.; Ahmad, R.; Thanh Tùng, Đ.; Knepper, I.; Villinger, A.; Langer, P. *Tetrahedron* **2011**, *67*, 5304–5318.
(11) Basaveswara Rao, M. V.; Satyanarayana, J.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1995**, *36*, 3385–3388.
(12) Nandin de Carvalho, H.; Dmitrienko, G. I.; Nielson, K. E. *Tetrahedron* **1990**, *46*, 5523–5532.
(13) Van Doren, P.; Compernolle, F.; Hoornaert, G. *Tetrahedron* **1990**, *46*, 4023–4030.
(14) Sings, H. L.; Harris, G. H.; Dombrowski, A. W. *J. Nat. Prod.* **2001**, *64*, 836–838.
(15) Exon, C.; Gallagher, T.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1982**, 613–614.
(16) Inagaki, F.; Mizutani, M.; Kuroda, N.; Mukai, C. *J. Org. Chem.* **2009**, *74*, 6402–6405.
(17) Kuroda, N.; Takahashi, R.; Yoshinaga, K.; Mukai, C. *Org. Lett.* **2006**, *8*, 1843–1845.
(18) Vice, S. F.; Nandin de Carvalho, H.; Taylor, N. G.; Dmitrienko, G. I. *Tetrahedron Lett.* **1989**, *30*, 7289–7292.
(19) Gagnon, D.; Spino, C. *J. Org. Chem.* **2009**, *74*, 6035–6041.
(20) Michelet, V.; Toullec, P. Y.; Genet, J. P. *Angew. Chem. Int. Ed.* **2008**, *47*, 4268–4315.
(21) Aubert, C.; Fensterbank, L.; Garcia, P.; Malacria, M.; Simonneau, A. *Chem. Rev.* **2011**, *111*, 1954–1993.
(22) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994–2009.
(23) Hashmi, A. S. K.; Yang, W.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 1273–1279.
(24) Modha, S. G.; Kumar, A.; Vachhani, D. D.; Jacobs, J.; Sharma, S. K.; Parmar, V. S.; Van Meervelt, L.; Van der Eycken, E. V. *Angew. Chem. Int. Ed.* **2012**, *51*, 9572–9575.
(25) Modha, S. G.; Vachhani, D. D.; Jacobs, J.; Van Meervelt, L.; Van der Eycken, E. V. *Chem. Commun.* **2012**, *48*, 6550–6552.
(26) Cera, G.; Chiarucci, M.; Mazzanti, A.; Mancinelli, M.; Bandini, M. *Org. Lett.* **2012**, *14*, 1350–1353.
(27) Cera, G.; Crispino, P.; Monari, M.; Bandini, M. *Chem. Commun.* **2011**, *47*, 7803–7805.
(28) Zhang, Y. Q.; Zhu, D. Y.; Jiao, Z. W.; Li, B. S.; Zhang, F. M.; Tu, Y. Q.; Bi, Z. *Org. Lett.* **2011**, *13*, 3458–3461.
(29) Wang, L.; Li, G.; Liu, Y. *Org. Lett.* **2011**, *13*, 3786–3789.
(30) Liu, Y. L.; Xu, W.; Wang, X. *Org. Lett.* **2010**, *12*, 1448–1451.
(31) Ferrer, C.; Escribano-Cuesta, A.; Echavarren, A. M. *Tetrahedron* **2009**, *65*, 9015–9020.
(32) Ferrer, C.; Amijs, C. H.; Echavarren, A. M. *Chem. Eur. J.* **2007**, *13*, 1358–1373.
(33) Ferrer, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 1105–1109.
(34) Chen, B.; Fan, W.; Chai, G.; Ma, S. *Org. Lett.* **2012**, *14*, 3616–3619.
(35) Zeldin, R. M.; Toste, F. D. *Chem. Sci.* **2011**, *2*, 1706–1709.

(36) Liu, C.; Widenhoefer, R. A. *Org. Lett.* **2007**, *9*, 1935−1938.
(37) Barluenga, J.; Piedrafita, M.; Ballesteros, A.; Suarez-Sobrino, A. L.; Gonzalez, J. M. *Chem. Eur. J.* **2010**, *16*, 11827−11831.
(38) Qiu, Y.; Ma, D.; Fu, C.; Ma, S. *Org. Biomol. Chem.* **2013**, *11*, 1666−1671.
(39) Kong, W.; Fu, C.; Ma, S. *Chem. Eur. J.* **2011**, *17*, 13134−13137.
(40) Alcaide, B.; Almendros, P.; Alonso, J. M.; Quirós, M. T.; Gadzin´ski, P. *Adv. Synth. Catal.* **2011**, *353*, 1871−1876.
(41) Kong, W.; Qiu, Y.; Zhang, X.; Fu, C.; Ma, S. *Adv. Synth. Catal.* **2012**, *354*, 2339−2347.
(42) Kong, W.; Fu, C.; Ma, S. *Org. Biomol. Chem.* **2012**, *10*, 2164−2173.
(43) Kong, W.; Fu, C.; Ma, S. *Chem. Commun.* **2009**, 4572−4574.
(44) Alcaide, B.; Almendros, P.; Alonso, J. M.; Fernandez, I. *Chem. Commun.* **2012**, *48*, 6604−6606.
(45) Sanz, R.; Álvarez, E.; Miguel, D.; García-García, P.; Fernández-Rodríguez, M.; Rodríguez, F. *Synthesis* **2012**, 1874−1884.
(46) Álvarez, E.; Miguel, D.; García-García, P.; Fernández-Rodríguez, M. A.; Rodríguez, F.; Sanz, R. *Beilstein J. Org. Chem.* **2011**, *7*, 786−793.
(47) Sanz, R.; Miguel, D.; Gohain, M.; García-García, P.; Fernández-Rodríguez, M. A.; González-Pérez, A.; Nieto-Faza, O.; de Lera, A. R.; Rodríguez, F. *Chem. Eur. J.* **2010**, *16*, 9818−9828.
(48) Sanz, R.; Miguel, D.; Rodríguez, F. *Angew. Chem. Int. Ed.* **2008**, *47*, 7354−7357.
(49) For an interesting recently study regarding the "silver effect" in gold(I) catalysis reported by Shi, see: Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012−9019.
(50) Sanz, R.; Miguel, D.; Martínez, A.; Gohain, M.; García-García, P.; Fernández-Rodríguez, M. A.; Álvarez, E.; Rodríguez, F. *Eur. J. Org. Chem.* **2010**, 7027−7039.
(51) Sanz, R.; Miguel, D.; Álvarez-Gutiérrez, J.; Rodríguez, F. *Synlett* **2008**, 975−978.
(52) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492−4493.
(53) Myers, A. G.; Zheng, B.; Movassaghi, M. *J. Org. Chem.* **1997**, *662*, 7507.
(54) Oku, M.; Arai, S.; Katayama, K.; Shioiri, T. *Synlett* **2000**, 493−494.
(55) The minor isomer was also isolated and characterized in the cases where it was formed in significant amount. See Experimental section.
(56) CCDC-934902 contains the supplementary crystallographic data for **2u**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
(57) The formation of species **7** could be supported by our previous theoretical and experimental studies on related reactions of 3-propargylindoles (ref. 45-48) whereas the role of spirocyclic complexes **8** as intermediates is well documented (see, for instance, ref. 23,32-33).