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Cycloaddition versus Alkylation Reactions of 2-Vinylindoles with α,β-Unsaturated Carbonyl Compounds Under Gold Catalysis

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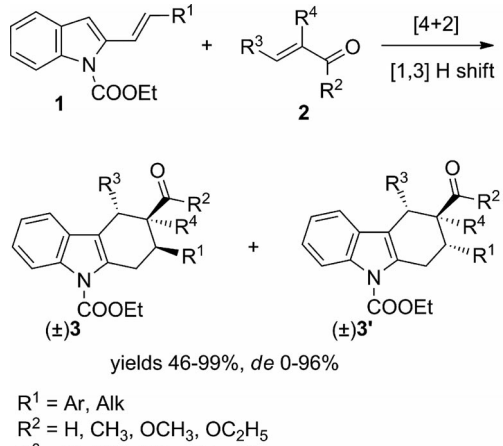
The gold-catalyzed intermolecular Diels–Alder cycloaddition and competitive Michael addition reactions between 2-vinylindoles and enones/enals are reported. The reaction outcome strictly correlates with the electronic character of the heteroaromatic substrate. Thus, Diels–Alder cycloadducts are the sole products in the presence of less electron-rich heterocycles, whereas Michael addition adducts are observed with more electron-rich heterocycles. Plausible competitive reaction mechanisms are proposed and discussed as well.

Introduction

The Diels–Alder (DA) reaction is one of the most powerful methods to build both simple and complex (poly)cyclic and (poly)heterocyclic compounds.[1] In addition to the simultaneous formation of two new carbon–carbon or carbon–heteroatom bonds, the success of the DA methodology is predominantly a result of the high regio-, diastereo-, and enantioselectivities observed. Excellent results, related to the reaction mechanism, are achieved by modifying the substituents of both the diene and dienophile as well as by the design and use of different catalytic species. Inter alia, many DA reactions are accelerated by Lewis acid (LA) catalysts, and catalyzed reactions often exhibit increased regio- and stereoselectivities in comparison to uncatalyzed ones.[2] On the other hand, it is worth noting that catalyzed reactions may produce different products as a result of the LA employed.[3] In particular, the DA reactions of internal-external ring dienes, which are derived from heterocyclic compounds, with activated C=C dienophiles represent an attractive approach to polyheterocyclic compounds.[1b–1d] In this context, 2-vinylindole species are useful partners in [4+2] cycloaddition reactions to provide easy access to complex tetrahydrocarbazole derivatives. Beginning with the pioneering works of Pindur,[4] the most recent findings include applications to the syntheses of composite carbazoles[5] and indole alkaloids such as (±)-3-*epi*-dasycarpidone,[6] pyrrolocarbazoles,[7] vinca alkaloids,[8] (+)-minfiensine,[9] and coumarin-fused tetrahydrocarbazoles.[10] In addition, we recently[11] described the DA cycloaddition reactions of (*E*)-2-vinylindole-1-carboxylic acid ethyl esters[12] **1** with C=C dienophiles **2**, (see Scheme 1). The reactions, which were performed in toluene in the presence of 15% of either magnesium perchlorate, scandium triflate, or boron trifluoride as the Lewis acid catalysts, proceeded to yield the expected diastereomeric cycloadducts (±)-**3** and (±)-**3′** with diastereoselectivities that ranged from poor to excellent, depending on the substitution pattern of both the dienes and dienophiles. In the same context, we recently described the synthesis of tetrahydrocarbazole derivatives through an intermolecular cycloaddition of vinyl indoles and *N*-allenamides under gold catalysis.[13]



Scheme 1. Diels–Alder reactions of 2-vinylindoles with C=C dienophiles.

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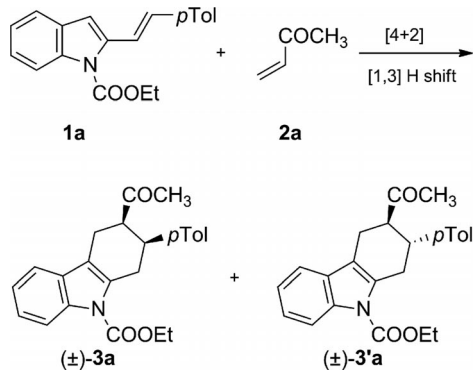
With the excellent reported results for copper-catalyzed DA reactions[14] and the recent gain in popularity of both silver- and gold-based catalysts,[15] we were curious to test the catalytic activity of the entire series of coinage metals in our intermolecular DA reactions. Coinage metal salts display σ- and π-philic properties to activate either the carbon–carbon or carbon–heteroatom multiple bonds.[16] Thus, testing their performance in our reactions appeared particularly attractive. Moreover, as the conjugate addition of activated alkenes to indoles under gold catalysis is a well-investigated reaction, the competitive formation of Michael-type adducts (MA)[17] would also be evaluated. The use of silver salts as a conventional LA in DA and aza-DA reactions has been reported for the reactions of several dienes with acrylonitriles[18] and imines,[19] respectively. Moreover, several studies that explore the oxophilic Lewis acidity of an Au species in 1,3-dipolar cycloaddition reactions have recently been published,[20] and cycloaddition reactions in which a gold catalyst activates the π-bonds have been recently reviewed.[21]

Results and Discussion

By using ethyl 2-[(*E*)-2-*p*-tolylvinyl]-1*H*-indole-1-carboxylate (**1a**)[11,12] and 3-buten-2-one (**2a**) in a model reaction, we tested a series of reaction conditions for the synthesis of tetrahydrocarbazoles (±)-**3a** and (±)-**3′a** (see Table 1).

In all of the experiments, *endo*-tetrahydrocarbazole (±)-**3a** was the main reaction product, and the Michael-type adduct was neither isolated nor observed by ^{1}H NMR analysis of the crude reaction mixture. Our previously reported results with $Mg(ClO_4)_2$[11a] are included in Table 1, Entry 1, and the results of the evaluation of scandium triflate (OTf) and boron trifluoride–diethyl ether, which were selected as the best catalysts for the DA reactions of 2-vinylindoles with cyclic C=C dienophiles,[11b] are listed in Table 1, Entries 2 and 3. In our model reaction, excellent yields were obtained with both catalysts, but better diastereoselectivity resulted when the reaction was performed in toluene at –20 °C with boron trifluoride–diethyl ether. Next, we tested the activity of the coinage metals. Both copper(I) and copper(II) triflate were active catalysts when dichloromethane was used as the solvent, whereas in toluene only copper(II) triflate was effective (see Table 1, Entries 4–7). The reactions could be performed at room temperature with a catalyst loading of 15 mol-%, and excellent yields and good diastereomeric excess values were achieved under these conditions. However, no reaction occurred with a catalyst loading of 5 mol-% under the conditions reported in Table 1, Entries 4–7. Silver triflate gave similar good results with a catalyst loading of 2 mol-% (see Table 1, Entry 8), whereas triphenylphosphane gold(I) chloride was ineffective (see Table 1, Entry 9). Cationic gold(I) complexes, which were generated in situ from triphenylphosphane gold(I) chloride and silver triflate or silver hexafluoroantimonate, provided better results (see Table 1, Entries 10 and 11) to give yields that ranged from 96 to 86% and *de* values from 86 to 89%. The effective catalyst was a cationic gold(I) species as suggested by the experiment performed with isolated triphenylphosphane gold(I) triflate[22] (see Table 1, Entry 12). Toluene seemed to be the solvent of choice, as the reaction that was performed in chloroform (see Table 1, Entry 13) resulted in a reduced yield and *de* value. As a consequence, we briefly explored several cationic gold species. The reaction that was performed in the presence of a bidentate phosphane ligand resulted in a marked decrease in diastereoselectivity (see Table 1, Entry 14), whereas the reaction that was carried out in the presence of a more coordinating counterion (i.e., NTf_2) was unsuccessful (see Table 1, Entry 15). Finally, the cationic species that was generated in situ from an N-heterocyclic

Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst [mol-%]	Solvent	*T* [°C]	*t* [h]	% Yield[b]	% *de*[c]
1	$Mg(ClO_4)_2$ (15)	toluene	110	24	77	43
2	$Sc(OTf)_3$ (15)	CH_2Cl_2	r.t.	24	95	67
3	$BF_3{\cdot}OEt_2$ (15)	toluene	–20	1.5	92	84
4	CuOTf (15)	toluene	r.t.	24	–	–
5	CuOTf (15)	CH_2Cl_2	r.t.	120	95	64[d]
6	$Cu(OTf)_2$ (15)	toluene	r.t.	96	81	71[d]
7	$Cu(OTf)_2$ (15)	CH_2Cl_2	r.t.	24	94	71
8	AgOTf (2)	toluene	r.t.	24	88	78
9	$Au(PPh_3)Cl$ (2)	toluene	r.t.	24	–	–
10	$Au(PPh_3)Cl$/AgOTf (2)	toluene	r.t.	24	96	86
11	$Au(PPh_3)Cl/AgSbF_6$ (2)	toluene	r.t.	24	86	89
12	$Au(PPh_3)OTf$ (2)	toluene	r.t.	24	93	86
13	$Au(PPh_3)Cl$/AgOTf (2)	$CHCl_3$	r.t.	24	83	75
14	$BINAP(AuCl)_2$[e]/ AgOTf (2)	toluene	r.t.	24	99	75
15	PPh_3AuNTf_2	toluene	r.t.	24	–	–
16	Au(IPr)Cl[e]/AgOTf (5)	toluene	80	48	61	75[d]
17	Au(IPr)Cl[e]/$AgSbF_6$ (5)	toluene	80	48	85	60[d]
18	$AuCl_3$ (2)	toluene	r.t.	1.5	99	85
19	$AuCl_3$ (2)	toluene	0	18	93	86
20	$PtCl_2$ (2)	toluene	r.t.	24	–	–

[a] For Entries 1, 2, and 4–20, a solution of the catalyst in the appropriate solvent (2 mL) was treated with **1a** (1 equiv.) and **2a** (1.2 equiv.). At the end, the solvent was removed, and the residue was purified by flash chromatography over silica gel. For Entry 3, see Exp. Section. [b] Yield of combined isolated DA products. [c] Diastereomeric excess (*de*) values determined using isolated products. [d] Calculated by ^{1}H NMR analysis of the *endo*/*exo* mixture. [e] BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene.

carbene (NHC) gold(I) chloride complex and silver triflate or silver hexafluoroantimonate were ineffective at room temperature but at 80 °C gave the corresponding tetrahydrocarbazoles in decreased yields and with moderate diastereoselectivities (see Table 1, Entries 16 and 17). Next, gold(III) chloride was tested at room temperature in toluene to give similar results with respect to $Au(PPh_3)Cl/AgOTf$ (see Table 1, cf. Entries 10 and 18), however, there was a tangible reduction in the reaction time. Lowering the reaction temperature to 0 °C did not affect yield or the diastereomeric ratio (see Table 1, Entry 19). A comparison between platinum and gold-based catalysts, in which the complementarity of electrophilic activation has been demonstrated,[23] was performed (see Table 1, Entry 20), but platinum chloride as a catalyst was ineffective.

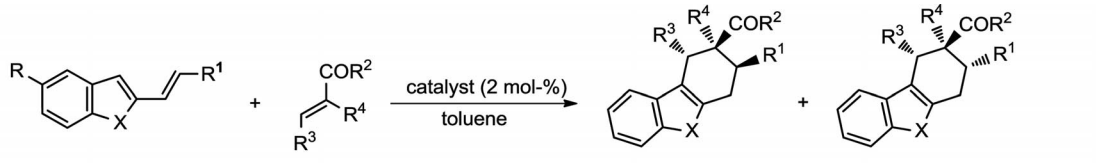
In most cases, the coinage metal catalysts gave better diastereomeric ratios than those obtained with magnesium perchlorate and scandium triflate, and these reactions proceeded faster or under milder conditions (see Table 1, Entries 1 and 2 vs. 7 and 8, 10–14, and 16–19). On the other hand, these results were comparable to those obtained under boron trifluoride catalysis. Although under coinage metal catalysis, the reactions could be performed at room temperature (see Table 1, Entries 3 vs. 10 and 18). Hence, upon comparing the reported results, we explored the scope of the reaction under the conditions in Table 1, Entries 10 and 18 by treating vinylindoles **1a**–**1f**[11–13] with a carbamate at N-1 and (*E*)-5-methoxy-2-(4-methylstyryl)benzofuran **4**[13] with alkenes **2a**–**2e** (see Table 2). The [4+2] cycloaddition reactions of 2-vinylbenzofurans with activated alkenes have been seldom reported in the literature[1c,24] but proceed under thermal or high pressure conditions with cyclic alkenones, tetracyanoethylene, and maleic anhydride.

In almost all reported experiments, tetrahydrocarbazoles (±)-**3** and (±)-**3′** were obtained in good to excellent overall yields. Once again, the Michael-type addition compounds were neither isolated nor detected. The diastereoselectivity for the *endo* product remained high with 2-vinylindoles that contained arenes with different electronic properties at the β-position (see Table 2, Entries 1 and 2). Moreover, nearly *endo* diastereospecific reactions were attained with β-alkyl-substituted vinylindoles **1d**–**1f** (see Table 2, Entries 3–5). In these latter reactions, a small percentage of regioisomeric 1,3-disubstituted tetrahydrocarbazoles **3′′a**–**3′′c** were also isolated as diastereomeric mixtures (see Table 2, Notes d and e).[25] The introduction of a phenyl group at the β-position of the dienophiles resulted in an almost complete loss of diastereoselectivity with both aryl and alkyl vinylindoles (see Table 2, Entries 6 and 7), and a higher reaction temperature was required when vinylindole **1e** was the substrate (see Table 2, Entry 7). A severe drop in the diastereoselectivity was also observed when crotonaldehyde and cinnamaldehyde were used as dienophiles (see Table 2, Entries 8 and 9), and once again the introduction of a phenyl group at the β-position of the dienophile resulted in the isolation of almost equimolar amounts of *endo*/*exo* cycloadducts (see Table 2, Entry 9). Finally, cyclic dienophile **2e** appeared less reactive (see Table 2, Entry 10). The reaction with cationic gold(I) at room temp. for 12 h and at 110 °C for 12 h gave rise to **3k/3′k** in good yield but with a poor *de* value, whereas the reaction with gold(III) chloride after 24 h at room temp. afforded **3k/3′k** in poorer yield but with a *de* value with the *exo* adduct as the main reaction product. The behavior of **4** with both gold(I) and gold(III) catalysts was similar to that of *N*-ethoxycarbonyl derivatives **1a**–**1f** and afforded 8-methoxy-2-acetyl-3-(*p*-tolyl)-1,2,3,4-tetrahydrodibenzo[*b*,*d*]furans **5** and **5′** in moderate overall yield and with a better *de* value in the presence of gold(III) chloride (see Table 2, Entry 11). In most of the experiments, the gold(III) chloride catalyst appeared to be superior to the cationic gold(I) catalyst and provided better yields and diastereomeric ratios. Only the reactions performed with **2b** gave similar results with both catalysts (see Table 2, Entries 6 and 7).

The structures of the diastereomeric cycloadducts **3** and **3′** were assigned on the basis of analytical and spectroscopic data. In particular, the combination of 1D [^{1}H NMR, attached proton test (APT)] and 2D (COSY, HETCOR) experiments, which were performed at 300 or 500 MHz, with C_6D_6 or $CDCl_3$ as solvents, allowed the complete assignment of chemical shifts and coupling constants. The regio- and stereochemistry of the DA adducts were assigned on the basis of spatial coupling interactions, which were detected by 2D NOE experiments.[11] Moreover, the structures and the *endo* stereochemistry of compounds **3f** and **5** were assigned on the same basis and unambiguously confirmed by X-ray diffraction analysis of a single crystal (see Supporting Information).

The reaction mechanism probably involves σ-activation of the dienophile by the metal, and the formation of the DA adduct could take place through a pseudoconcerted or a fast stepwise mechanism (see Scheme 2).[4] In the fast stepwise path, the driving force to the exclusive formation of the cycloaddition products, which avoids the formation of the Michael-type adducts, could be related to the presence of the carbamate substituent on the indole. This can lower the nucleophilic character of the indole nitrogen, and thus the relative contribution of intermediate **IB** with respect to **IC** results in the enhanced electrophilic character of the outer carbon atom of the vinyl system. Similar concerns account for the results obtained with compound **4**. Additionally, the observed *endo*/*exo* ratios could be rationalized as reported for common LA-catalyzed DA reactions. Thus, LA-catalyzed cycloadditions proceed faster than their thermal counterparts and are often more regio- and stereoselective, depending on the LA employed. In our experience, the *endo* diastereoselectivity for the reactions of indole-*N*-carbamates **1a**–**1f** with β-unsubstituted dienophiles **2a** and **2c** remains consistently high or specific, which is a result best explained through FMO theory.[1] The loss of diastereoselectivity that is observed in the reactions with dienophiles **2b** and **2d** is probably because of secondary orbital interactions (SOI) between the β-phenyl substituent of the dienophile and the π-system of the diene, with a consequent decrease in the energy difference between the *endo* and *exo* transition states.[1] When the C=C double bond of

Table 2. Scope of the [4+2] cycloaddition reactions of 2-vinyl-substituted heterocycles with electrophilic alkenes.[a]

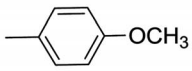
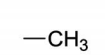
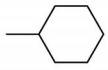
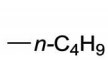
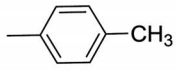
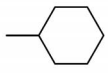
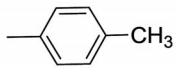
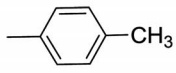
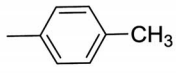
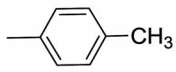


1a–f, X = N-COOEt, R = H
4, X = O, R = OCH_3

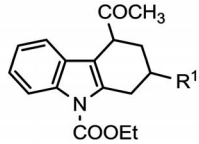
2a–e

(±)-**3b–k**, X = N-COOEt (R = H)
(±)-**5**, X = O (R = OCH_3)

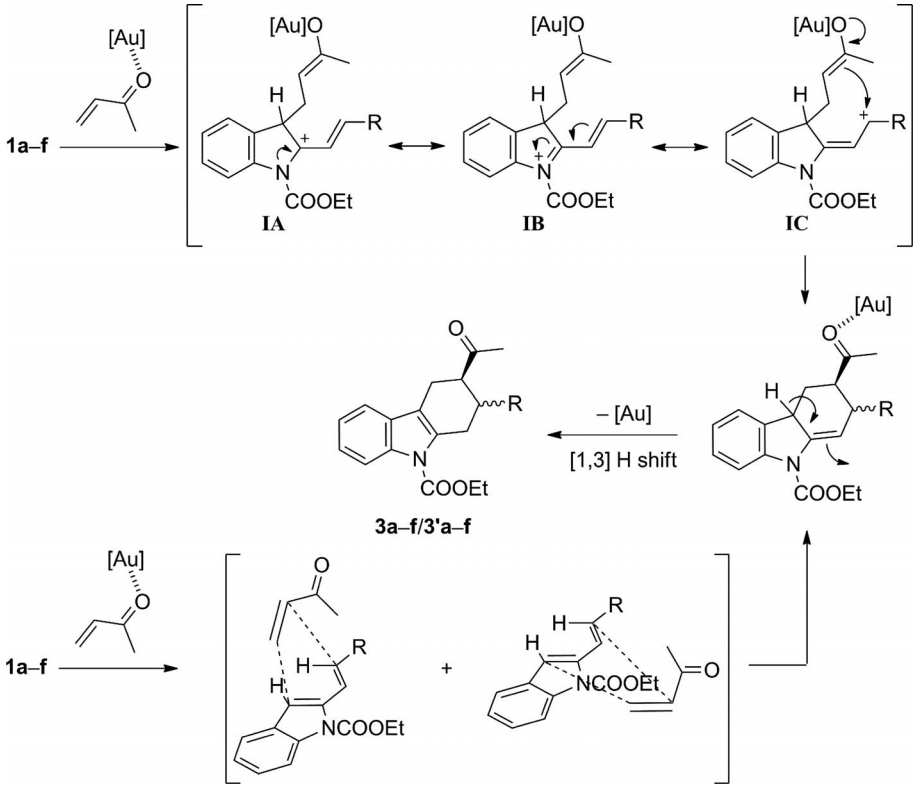
(±)-**3'b–k**, X = N-COOEt
(±)-**5'**, X = O

Entry	1/4	R^1	2	R^2	R^3	R^4	3/5	Catalyst [2 mol-%]	Time [h]	Yield [%][b]	*de* [%][c]
1	**1b**		**2a**	CH_3	H	H	**3b/3'b**	$Au(PPh_3)Cl/AgOTf$	24	89	80
								$AuCl_3$	1.5	91	87
2	**1c**		**2a**	CH_3	H	H	**3c/3'c**	$Au(PPh_3)Cl/AgOTf$	24	94	75
								$AuCl_3$	18	62	96
3	**1d**		**2a**	CH_3	H	H	**3d/3'd**	$Au(PPh_3)Cl/AgOTf$	24	93[d]	96
								$AuCl_3$	2	99[e]	> 98
4	**1e**		**2a**	CH_3	H	H	**3e**	$Au(PPh_3)Cl/AgOTf$	28	80[d]	> 98
								$AuCl_3$	3	95[e]	> 98
5	**1f**		**2a**	CH_3	H	H	**3f**	$Au(PPh_3)Cl/AgOTf$	24	82[d]	> 98
								$AuCl_3$	5	62[e,f]	> 98
6	**1a**		**2b**	CH_3	Ph	H	**3g/3'g**	$Au(PPh_3)Cl/AgOTf$	24	84	–2
								$AuCl_3$	1.5	86	0
7	**1e**		**2b**	CH_3	Ph	H	**3h/3'h**	$Au(PPh_3)Cl/AgOTf$	65[g]	53[h]	0
								$AuCl_3$	65[g]	38[i]	15
8	**1a**		**2c**	H	H	H	**3i/3'i**	$Au(PPh_3)Cl/AgOTf$	24	89	46
								$AuCl_3$	1.5	96	60
9	**1a**		**2d**	H	Ph	H	**3j/3'j**	$Au(PPh_3)Cl/AgOTf$	24	70	9
								$AuCl_3$	48	62[j]	33
10	**1a**		**2e**	H	-$(CH_2)_3$-		**3k/3'k**	$Au(PPh_3)Cl/AgOTf$	24[k]	81[l]	13
								$AuCl_3$	24	24[m]	–50
11	**4**		**2a**	CH_3	H	H	**5/5'**	$Au(PPh_3)Cl/AgOTf$	24	61[n]	57
								$AuCl_3$	24	51[o]	91

3''a: $R^1 = CH_3$
3''b: R^1 = cyclohexyl
3''c: $R^1 = n\text{-}C_4H_9$



[a] Heterocycle **1** (1 equiv.) and alkene **2** (1.2 equiv.). [b] Yield of combined isolated products. [c] Diasteromeric excess values determined using isolated products. [d] Given yields include 5, 6, and 10%, respectively, of regioisomeric **3''a**, $R^1 = CH_3$; **3''b**, R^1 = cyclohexyl; **3''c**, $R^1 = n\text{-}C_4H_9$ (unresolved mixture of diastereomers). [e] Given yields include 3, 8, and 7%, respectively, of regioisomeric **3''a**–**3''c**. [f] Recovered **1f**, 25%. [g] At room temp. for 48 h and at 80 °C for 17 h. [h] Along with a mixture of unidentified tarry compounds. [i] Recovered **1e**, 50%. [j] Recovered **1a**, 25%. [k] At room temp. for 12 h and at 110 °C for 12 h. [l] Recovered **1a**, 18%. [m] Recovered **1a**, 50%. [n] Recovered **4**, 18%. [o] Recovered **4**, 27%.



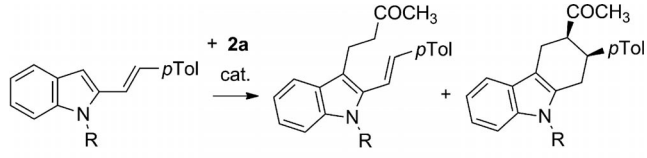
Scheme 2. Proposed mechanisms for DA cycloadditions.

the dienophile is secured as part of a cycle, as in **2e**, the obtained results are erratically distributed and difficult to rationalize, which suggests that additional factors such as steric and electrostatic effects, closed-shell repulsions, and secondary orbital interactions could be operative.

All these observations are in agreement with the results from a second set of experiments in which the electronic properties of the heterocyclic system were evaluated. Thus, we explored the reactivity of the (*E*)-*N*-unsubstituted and (*E*)-*N*-methyl-2-vinylindoles **1g** and **1h**[13] in reactions with methyl vinyl ketone (MVK) **2a** (see Table 3). A comparison of the reactions with cationic gold(I), gold(III), and BF_3 as catalysts was accomplished. *N*-unsubstituted 2-vinylindoles are reported to react thermally with electrophilic acyclic alkenes or in the presence of silica gel or molecular sieves to yield the single *endo* diastereomer, although in low yield.[4]

The reactions performed with **1g** gave poor results with all of the catalysts, and the Michael-type addition product **6a** was always isolated along with DA adduct **3l**, which was obtained as a single diastereomer (see Table 3, Entries 1–3). Working with **1h** under boron trifluoride or cationic gold(I) catalysis, the DA cycloadduct **3m** was obtained in high yields and with complete diastereoselectivity (see Table 3, Entries 4 and 5). Conversely, the reaction of **1h** under gold(III) catalysis furnished a mixture of **6b** and **3m** (as a single diastereomer, see Table 3, Entry 6). Therefore, the Michael-type addition and the Diels–Alder reaction were in competition when the more electron-rich 2-vinyl-1*H*-indole **1g** was employed. When **1h** was used, the reaction type was dependent on the catalyst employed. However, compounds **6a** and **6b** could arise from a Friedel–Craft-type of reaction or involve the C–H activation of the heteroaromatic system as reported in Sche of the well-known σ-acidity of boron trifluoride, Path A is effective under boron catalysis, and the

Table 3. Reactivity of vinylindoles **1g** and **1h** with MVK **2a**.[a,b]



1g, R = H
1h, R = CH_3
6a, R = H
6b, R = CH_3
(±)-**3l**, R = H
(±)-**3m**, R = CH_3

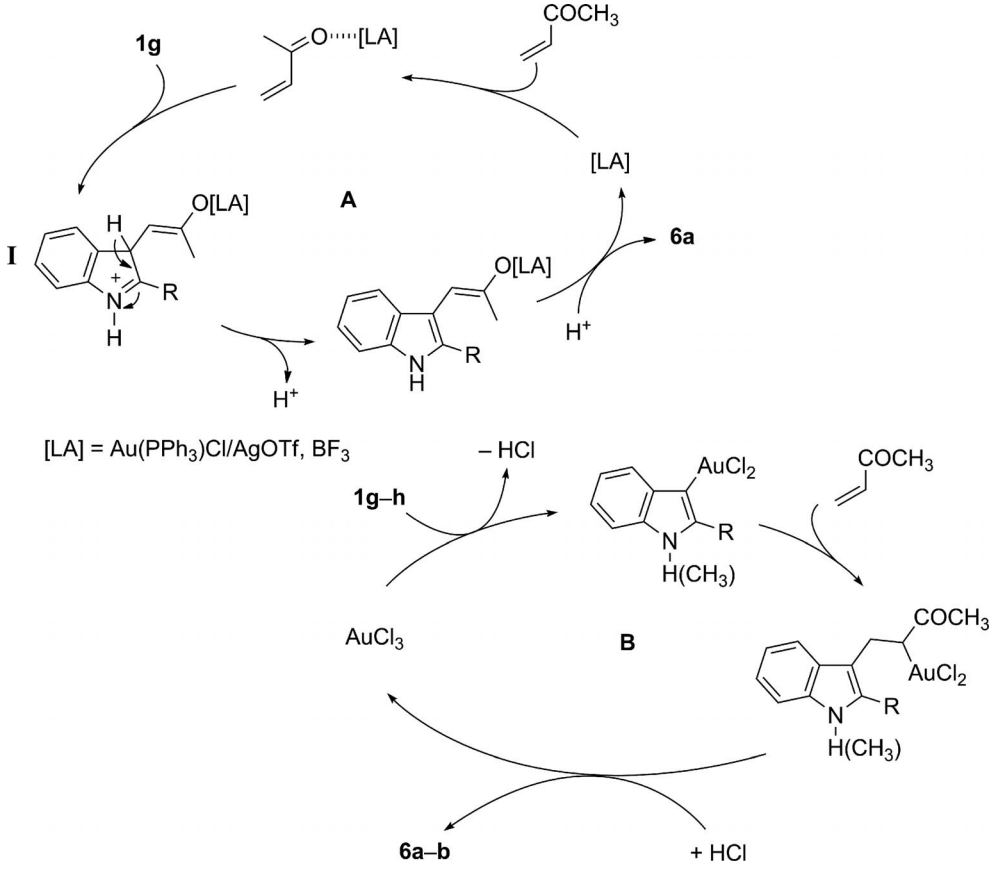
Entry	1	Catalyst [mol-%]	*T* [h]	Overall yield [%]	MA [%]	DA [%]	*de*[c] [%]
1	**1g**	BF_3·OEt_2 (15)	2.5	28[d]	11	17	>99
2	**1g**	Au(PPh_3)Cl/AgOTf (2)	24	62[e]	44	18	>99
3	**1g**	$AuCl_3$ (2)	24	76	58	18	>99
4	**1h**	BF_3·OEt_2 (15)	4	80	trace	80	>99
5	**1h**	Au(PPh_3)Cl/AgOTf (2)	24	72	trace	72	>99
6	**1h**	$AuCl_3$ (2)	24	77[f]	57	20	>99

[a] Heterocycle **1** or **4** (1 equiv.) and **2** (1.2 equiv.), toluene, room temp. [b] Heterocycle **1** (1 equiv.) and **2** (1.5 equiv.), CH_2Cl_2, –20 °C. [c] Diastereomeric excess values determined using isolated products. [d] Along with a mixture of unidentified tarry compounds. [e] Recovered **1g**, 20%. [f] Recovered **1h**, 14%.

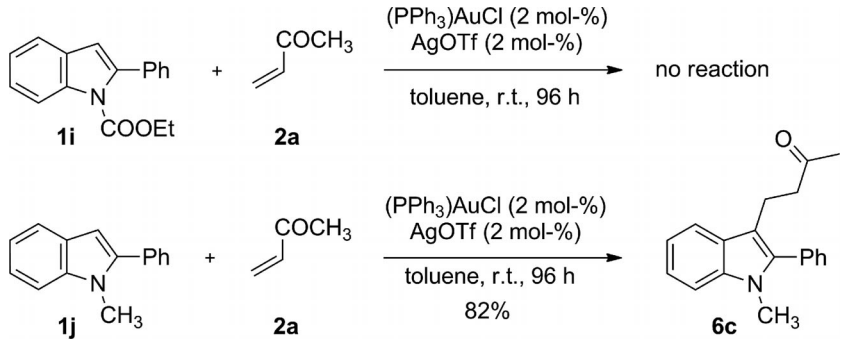
behaviors of **1g** and **1h** (relative yields of **6a/6b** vs. **3l/3m**) reflect the relative reaction rate of the MA with respect to the DA reaction of *N*-unsubstituted and *N*-alkyl-substituted indoles, with the latter being less reactive than the former. On the other hand, a mechanism involving C–H activation (see Scheme 3, Path B) of te heteroaromatic system could not be a priori excluded under gold(III) catalysis, as suggested by several authors.[26] Nevertheless, under gold(I) catalysis, the C_{sp^2}–H bond activation has been demonstrated to be consistent only for electron-deficient substrates.[27] Moreover, 3-benzofuranyl- and 3-indolyl-gold(I) derivatives have been isolated and characterized by Hashmi as stable intermediates of gold(I)-catalyzed hydroxylation and hydroamination reactions of *ortho*-alkynylphenols and anilines. However, they easily undergo deauration reactions and cannot be prepared from the corresponding benzofuran or indole derivatives and gold(I).[28] On the contrary, the oxophilic character of gold(I) species has been highlighted by several authors, in particular by Toste with regard to gold(I)-catalyzed Mannich reactions of azalactones[20a] and by Youn with regard to the gold(I)-catalyzed intramolecular cyclizations of 2-alkenyl carbonyl compounds.[29] Thus, considering our results, we could reasonably disregard, a mechanism involving a C_{sp^2}–H activation step under gold(I) catalysis, and because of the well-known σ-acidity of cationic gold(I) species, a Friedel–Crafts-type mechanism could more realistically explain the formation of the observed MA products (see Scheme 3, Path A).

It is interesting to note that the mechanisms described in Scheme 3, Path A and in Scheme 2 share the same type of cationic intermediate **I**, and the reactivity seems to be modulated by the relative stability of **I**. For the *N*-carbamate- and the O-heterocycle, the outer C atom of the vinyl system in intermediate **I** became a stronger acceptor with respect to the same intermediate generated from the N–H substrate, for which a fast deprotonation/rearomatization of the heterocyclic ring could occur. Finally, indirect support to our hypothesis was obtained by the reactions with either ethyl 2-phenyl-1*H*-indole-1-carboxylate (**1i**) or 1-methyl-2-phenyl-1*H*-indole (**1j**) and MVK **2a** in toluene at room temperature in the presence of $Au(PPh_3)Cl/AgOTf$ (2 mol-%, see Scheme 4). Under these conditions, **1i** was recovered from the reaction mixture even after a prolonged time (96 h), whereas **1j** furnished the corresponding 3-alkylated indole **6c** in 82% yield.

These findings appear to confirm our hypothesis that less electron-rich heterocycles are the substrates of choice to achieve the DA adducts selectively, and a reaction pathway that involves a simple addition to an α,β-unsaturated compound is not allowed.



Scheme 3. Plausible reaction mechanisms for MA reactions.



Scheme 4. Alkylation of indoles under cationic gold(I) catalysis.

Conclusions

This work compared the efficiency of coinage metal salts and complexes to traditional Lewis acid as catalysts in intermolecular DA reactions of vinyl heterocycles with activated alkenes. The most efficient catalysts were the cationic gold(I) complex $Au(PPh_3)Cl/AgOTf$ and gold(III) chloride, which gave results comparable to those obtained with the best performing traditional LA (boron trifluoride–diethyl ether). The only benefit was that the reactions with the coinage metals were performed at room temperature instead of at –20 °C, which was necessary with boron trifluoride. Despite this, by exploring the scope of the reaction, we were able to realize the synthesis of new compounds that are useful in medicinal and natural product chemistry. Moreover, the results reported in this study describe and point out several features about the reactivity of 2-vinyl heteroaromatics and α,β-unsaturated carbonyl compounds under gold catalysis. In all the studied reactions, the gold catalysts acted as an effective σ-philic Lewis acid that was able to activate the enone/enal partner. However, the final outcome of the reaction (DA vs. MA adduct) seemed to be mainly governed by the relative stability of the cationic aurate intermediate **I**. Moreover, we highlighted that conceivably the two catalysts assumed different behaviors in the presence of more electron-rich heterocycles and act as C–H or as σ-activators.

Experimental Section

General Methods: All chemicals and solvents were commercially available and used after distillation or treatment with drying agents. Silica gel F254 thin layer plates were employed for thin layer chromatography (TLC). Silica gel 40–63 micron/60 Å was employed for flash column chromatography. Melting points were measured with a Perkin–Elmer DSC 6 calorimeter at a heating rate of 5 °C/min. Infrared spectra were recorded with a Perkin–Elmer FTIR 16 PC spectrometer using KBr tablets or NaCl dishes. The ^1H and ^{13}C NMR spectroscopic data were recorded with a Varian-Gemini 200, a Bruker 300, or a Bruker 500 Avance spectrometer at room temperature. $CDCl_3$ or C_6D_6 were used as the solvent, and the residual solvent peaks were used as the internal reference. The APT sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. Two-dimensional NMR experiments [COSY, heteronuclear correlation (HETCOR), NOESY] were used, where appropriate, to aid in the assignment of structures. Low-resolution MS spectra were recorded with a Thermo-Finnigan LCQ advantage AP electrospray/ion trap-equipped instrument using a syringe pump device to directly inject the sample solutions. 1-Methyl-2-phenyl-1*H*-indole (**1j**) was commercially available and was used as purchased. 2-Vinylindoles **1a**–**1h** and 2-vinylbenzofuran **4** are known compounds.[11–13] CCDC-934078 and -934079 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ethyl 2-Phenyl-1*H*-indole-1-carboxylate (1i): To a suspension of NaH (60% in mineral oil, 208 mg, 5.2 mmol) in tetrahydrofuran (THF, 10 mL) was added 2-phenyl-1*H*-indole (0.5 g, 2.6 mmol) at 0 °C, and the mixture was stirred for 30 min. Then, ethyl chloroformate (423 mg, 0.373 mL, 3.9 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 4 h. After that time, water (10 mL) was slowly added, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under vacuum to yield **1i** (0.629 g, 91%), which was used without any further purification, as a white solid; m.p. 38.1–38.7 °C. IR (KBr): $\tilde{\nu}$ = 3051, 2991, 2905, 1729, 1562, 1456, 1376, 1328, 1222 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.24 (d, J = 8.4 Hz, 1 H), 7.59 (m, 1 H), 7.57–7.25 (m, 7 H), 6.62 (s, 1 H), 4.23 (q, J = 7.0 Hz, 2 H), 1.12 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 151.9 (C_q), 140.8 (C_q), 137.5 (C_q), 134.7 (C_q), 129.7 (C_q), 129.1 (CH), 128.0 (CH), 127.9 (CH), 124.7 (CH), 123.4 (CH), 120.8 (CH), 115.7 (CH), 110.8 (CH), 63.2 (CH_2), 13.9 (CH_3) ppm. MS (ESI+): m/z (%) = 266 (100) $[M + 1]^+$.

1-Methyl-2-phenyl-1*H*-indole (1j):[13] To a suspension of NaH (60% in mineral oil, 0.11 mg, 2.86 mmol) in dry *N*,*N*-dimethylformamide (DMF, 5 mL) was added 2-phenyl-1*H*-indole (0.5 g, 2.6 mmol) at 0 °C, and the mixture was stirred for 30 min. Then, methyl iodide (369 mg, 0.163 mL, 2.6 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 24 h. After that time, water (20 mL) was slowly added, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under vacuum to yield **1j** (0.485 g, 90%), which used without any further purification, as a white solid; m.p. 99–101 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.68–7.12 (m, 9 H), 6.57 (s, 1 H), 3.76 (s, 3 H) ppm.

General Procedure for Gold-Catalyzed [4+2] Cycloaddition Reactions: To a solution of either $AuPPh_3Cl$ (2.0 mol-%) and AgOTf (2.0 mol-%) or $AuCl_3$ (2.0 mol-%) in toluene (1 mL/0.2 mmol of catalyst) were added dienes **1a**–**1h** or **4** (1.0 equiv.) and dienophiles

2a–**2e** (1.2 or 2.4 equiv.), and the solution was stirred at the appropriate temperature for the stated time. The solvent was then removed in vacuo, and the residue was purified by flash column chromatography over silica gel.

General Procedure for BF_3·OEt_2-Catalyzed [4+2] Cycloaddition Reactions: To a nitrogen-flushed solution of **1a** or **1g**–**1h** (1.0 equiv.) and **2a** (1.5 equiv.) in toluene (1 mL/0.2 mmol) was added BF_3·OEt_2 (15 mol-%) at –20 °C, and the mixture was stirred at the same temperature for the stated time. The solvent was then removed in vacuo, and the residue was purified by flash column chromatography over silica gel.

Reactions of 1a and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.3 mg, 0.0066 mmol), AgOTf (1.7 mg, 0.0066 mmol), (*E*)-ethyl 2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1a**, 100 mg, 0.33 mmol) and 3-buten-2-one (**2a**, 27.8 mg, 0.40 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 98:2–95:5) progressively yielded **3′a** (8 mg, 7%) and **3a** (110 mg, 89%). The same general procedure was performed using $AuCl_3$ (2.0 mg, 0.0066 mmol) at room temperature for 1.5 h to yield **3′a** (9 mg, 7%) and **3a** (114 mg, 92%).

(±)-(*trans*)-Ethyl 3-Acetyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′a):[11a] White solid; m.p. 165.9–166.2 °C. IR (KBr): $\tilde{\nu}$ = 3052, 2916, 2849, 1723 cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ = 8.63 (d, *J* = 8.2 Hz, 1 H), 7.47 (m, 2 H), 7.38 (m, 1 H), 7.08 (d, *J* = 7.9 Hz, 2 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 4.23 (m, 2 H), 3.44 (dd, *J* = 5.0, 17.5 Hz, 1 H), 3.19 (ddd, *J* = 5.0, 10.5, 10.5 Hz, 1 H), 3.10 (dd, *J* = 10.5, 17.5 Hz, 1 H), 2.93 (ddd, *J* = 4.0, 10.5, 10.5 Hz, 1 H), 2.87 (dd, *J* = 10.5, 15.6 Hz, 1 H), 2.76 (dd, *J* = 4.0, 15.6 Hz, 1 H), 2.21 (s, 3 H), 1.72 (s, 3 H), 0.99 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, C_6D_6): δ = 209.0 (C_q), 151.6 (C_q), 140.7 (C_q), 136.5 (C_q), 136.2 (C_q), 134.4 (C_q), 129.6 (C_q), 129.4 (CH), 128.0 (CH), 124.1 (CH), 123.0 (CH), 117.8 (CH), 115.2 (CH), 115.2 (C_q), 62.4 (CH_2), 52.4 (CH), 43.6 (CH), 33.9 (CH_2), 29.7 (CH_3), 24.5 (CH_2), 20.8 (CH_3), 19.3 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 376 (40) $[M + 1]^+$, 304 (100).

(±)-(*cis*)-Ethyl 3-Acetyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3a):[11a] White solid; m.p. 141.6–142.7 °C. IR (KBr): $\tilde{\nu}$ = 3054, 2921, 1722, 1701 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 8.61 (d, *J* = 8.3 Hz, 1 H), 7.32–7.50 (m, 3 H), 6.96 (d, *J* = 7.9 Hz, 2 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 4.1 (q, *J* = 7.1 Hz, 2 H), 3.80 (dd, *J* = 4.0, 17.6 Hz, 1 H), 3.55 (ddd, *J* = 4.0, 4.0, 6.6 Hz, 1 H), 3.50 (dd, *J* = 6.6, 17.6 Hz, 1 H), 2.98 (dd, *J* = 7.3, 18.1 Hz, 1 H), 2.80 (m, 1 H), 2.78 (dd, *J* = 5.5, 18.1 Hz, 1 H), 2.14 (s, 3 H), 1.83 (s, 3 H), 1.02 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, C_6D_6): δ = 209.0 (C_q), 152.4 (C_q), 139.6 (C_q), 137.1 (C_q), 136.6 (C_q), 135.1 (C_q), 130.1 (C_q), 129.6 (CH), 127.9 (CH), 124.5 (CH), 123.4 (CH), 118.3 (CH), 116.5 (CH), 116.1 (C_q), 62.8 (CH_2), 51.5 (CH), 41.2 (CH), 31.7 (CH_2), 30.4 (CH_3), 29.3 (CH_3), 21.1 (CH_2), 14.2 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 376 (25) $[M + 1]^+$, 304 (100), 100 (70).

Reactions of 1b and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.2 mg, 0.0064 mmol), AgOTf (1.6 mg, 0.0064 mmol), (*E*)-ethyl 2-(4-fluorostyryl)-1*H*-indole-1-carboxylate (**1b**, 100 mg, 0.32 mmol), and 3-buten-2-one (**2a**, 27.0 mg, 0.38 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 98:2–95:5) progressively yielded **3′b** (11 mg, 9%) and **3b** (97 mg, 80%). The same general procedure was performed using $AuCl_3$ (1.9 mg, 0.0064 mmol) at room temperature for 1.5 h to yield **3′b** (7 mg, 6%) and **3b** (104 mg, 85%).

(±)-(*trans*)-Ethyl 3-Acetyl-2-(4-fluorophenyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′b): White solid; m.p. 161.7–161.9 °C. IR (KBr): $\tilde{\nu}$ = 3447, 2917, 2849, 1735, 1212 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.1 Hz, 1 H), 7.43 (d, *J* = 7.1 Hz, 1 H), 7.35–7.26 (m, 4 H), 7.06–7.03 (m, 2 H), 4.48 (q, *J* = 7.1 Hz, 2 H), 3.52 (dd, *J* = 4.9, 18.2 Hz, 1 H), 3.35 (ddd, *J* = 5.5, 10.5, 21.0 Hz, 1 H), 3.23 (ddd, *J* = 5.5, 10.5, 21.0 Hz, 1 H), 3.14 (m, 1 H), 2.99 (m, 1 H), 2.93 (m, 1 H), 1.97 (s, 3 H), 1.46 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 210.4 (C_q), 161.0 (d, $^1J_{C,F}$ = 245 Hz, C_q), 151.2 (C_q), 138.1 (d, $^4J_{C,F}$ = 4 Hz, C_q), 135.2 (C_q), 133.4 (C_q), 128.4 (d, $^3J_{C,F}$ = 8 Hz, CH), 128.3 (C_q), 123.4 (CH), 122.3 (CH), 117.0 (CH), 115.0 (CH), 114.9 (d, $^2J_{C,F}$ = 21 Hz, CH), 114.3 (C_q), 62.3 (CH_2), 52.2 (CH), 42.4 (CH), 32.7 (CH_2), 29.5 (CH_3), 23.6 (CH_2), 13.7 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 380 (100) $[M + 1]^+$. $C_{23}H_{22}FNO_3$ (379.42): calcd. C 72.81, H 5.84, N 3.69; found C 72.78, H 5.81, N 3.72.

(±)-(*cis*)-Ethyl 3-Acetyl-2-(4-fluorophenyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3b): White solid; m.p. 151.7–152.2 °C. IR (KBr): $\tilde{\nu}$ = 3424, 2920, 2849, 1721, 1702, 1209 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.2 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.33 (m, 2 H), 7.10 (m, 2 H), 6.93 (m, 2 H), 4.52 (m, 2 H), 3.82 (m, 1 H), 3.61 (m, 1 H), 3.54 (m, 1 H), 3.17 (m, 1 H), 2.95 (dd, *J* = 5.3, 16.6 Hz, 1 H), 2.84 (m, 1 H), 2.17 (s, 3 H), 1.51 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 208.7 (C_q), 161.1 (d, $^1J_{C,F}$ = 245 Hz, C_q), 151.3 (C_q), 136.5 (d, $^4J_{C,F}$ = 3 Hz, C_q), 135.5 (C_q), 133.5 (C_q), 128.7 (d, $^3J_{C,F}$ = 8 Hz, CH), 128.5 (C_q), 123.4 (CH), 122.3 (CH), 117.1 (CH), 115.0 (CH), 114.9 (C_q), 114.6 (d, $^2J_{C,F}$ = 21 Hz, CH), 62.3 (CH_2), 50.6 (CH), 39.6 (CH), 30.7 (CH_2), 28.8 (CH_3), 19.5 (CH_2), 13.7 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 380 (100) $[M + 1]^+$, 355 (40), 279 (30). $C_{23}H_{22}FNO_3$ (379.42): calcd. C 72.81, H 5.84, N 3.69; found C 72.73, H 5.76, N 3.62.

Reactions of 1c and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.1 mg, 0.0062 mmol), AgOTf (1.6 mg, 0.0062 mmol), (*E*)-ethyl 2-(4-methoxystyryl)-1*H*-indole-1-carboxylate (**1c**, 100 mg, 0.31 mmol), and 3-buten-2-one (**2a**, 26.0 mg, 0.37 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 98:2–95:5) progressively yielded **3′c** (14 mg, 12%) and **3c** (100 mg, 82%). The same procedure was performed using $AuCl_3$ (1.9 mg, 0.0062 mmol) at room temperature for 18 h to yield **3′c** (2 mg, 1%) and **3c** (104 mg, 61%).

(±)-(*trans*)-Ethyl 3-Acetyl-2-(4-methoxyphenyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′c): Yellow solid; m.p. 161.2–162.8 °C. IR (KBr): $\tilde{\nu}$ = 3436, 2918, 1724, 1703, 1513, 1211, 1031 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 7.7 Hz, 1 H), 7.34–7.26 (m, 2 H), 7.23 (m, 2 H), 6.90 (m, 2 H), 4.47 (q, *J* = 7.1 Hz, 2 H), 3.83 (s, 3 H), 3.50 (dd, *J* = 5.2, 18.1 Hz, 1 H), 3.28 (ddd, *J* = 5.2, 10.5, 21.0 Hz, 1 H), 3.21 (m, 1 H), 3.16 (m, 1 H), 2.94 (m, 2 H), 1.94 (s, 3 H), 1.45 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 210.9 (C_q), 157.8 (C_q), 151.2 (C_q), 135.3 (C_q), 134.3 (C_q), 133.7 (C_q), 128.4 (C_q), 128.0 (CH), 123.3 (CH), 122.2 (CH), 117.0 (CH), 114.9 (CH), 114.4 (C_q), 113.4 (CH), 62.2 (CH_2), 54.6 (CH), 52.4 (CH_3), 42.5 (CH), 32.8 (CH_2), 29.5 (CH_3), 23.6 (CH_2), 13.7 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 392 (20) $[M + 1]^+$, 414 (25) $[M + Na]^+$. $C_{24}H_{25}NO_4$ (391.46): calcd. C 73.64, H 6.44, N 3.58; found C 73.61, H 6.40, N 3.62.

(±)-(*cis*)-Ethyl 3-Acetyl-2-(4-methoxyphenyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3c): Yellow solid; m.p. 167.8–168.8 °C. IR (KBr): $\tilde{\nu}$ = 3430, 2909, 1724, 1699, 1611, 1512, 1339, 1251 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.1 Hz, 1 H), 7.48

(d, J = 7.2 Hz, 1 H), 7.35–7.28 (m, 2 H), 7.05 (d, J = 8.7 Hz, 2 H), 6.78 (m, 2 H), 4.51 (m, 2 H), 3.81 (m, 1 H), 3.77 (s, 3 H), 3.60 (m, 1 H), 3.52 (m, 1 H), 3.16 (m, 1 H), 2.93 (dd, J = 5.2, 16.6 Hz, 1 H), 2.85 (m, 1 H), 2.17 (s, 3 H), 1.50 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 209.1 (C_q), 157.8 (C_q), 151.3 (C_q), 135.5 (C_q), 133.7 (C_q), 132.8 (C_q), 128.6 (C_q), 128.1 (CH), 123.3 (CH), 122.2 (CH), 117.1 (CH), 115.0 (C_q), 114.9 (CH) 113.1 (CH), 62.2 (CH_2), 54.5 (CH), 50.8 (CH_3), 39.6 (CH), 30.8 (CH_2), 28.8 (CH_3), 19.4 (CH_2), 13.7 (CH_3) ppm. MS (ESI+): m/z (%) = 392 (10) $[M + 1]^+$, 414 (100) $[M + Na]^+$. $C_{24}H_{25}NO_4$ (391.46): calcd. C 73.64, H 6.44, N 3.58; found C 73.60, H 6.42, N 3.60.

Reactions of 1d and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (4.3 mg, 0.0086 mmol), AgOTf (2.2 mg, 0.0086 mmol), (*E*)-ethyl 2-propenylindole-1-carboxylate (**1d**, 100 mg, 0.43 mmol), and 3-buten-2-one (**2a**, 36.2 mg, 0.51 mmol) at room temperature for 24 h. Purification of the residue (toluene/hexane, 92:8) progressively yielded **3′′a** (7 mg, 5%), **3′d** (2 mg, 2%), and **3d** (111 mg, 86%). The same procedure was performed using $AuCl_3$ (2.6 mg, 0.0086 mmol) at room temperature for 2 h to yield **3′′a** (4 mg, 3%) and **3d** (126 mg, 96%).

Ethyl 4-Acetyl-2-methyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′′a):[11a,25] Yellow oil. IR (neat): $\tilde{\nu}$ = 3076, 2953, 2917, 2884, 1735, 1703 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, major diastereomer): δ = 8.50 (d, J = 8.3 Hz, 1 H), 7.49 (d, J = 7.6 Hz, 1 H), 7.32 (m, 2 H), 4.14 (q, J = 7.1 Hz, 2 H), 3.83 (m, 1 H), 3.17 (m, 1 H), 2.50 (ddd, J = 3.0, 10.8, 17.9 Hz, 1 H), 1.88 (s, 3 H), 1.80 (m, 1 H), 1.57 (m, 1 H), 1.27 (t, J = 12.2 Hz, 1 H), 1.06 (t, J = 7.1 Hz, 3 H), 0.95 (d, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, C_6D_6, major diastereomer): δ = 208.7 (C_q), 151.9 (C_q), 137.4 (C_q), 136.8 (C_q), 129.3 (C_q), 124.4 (CH), 123.6 (CH), 118.8 (CH), 116.3 (CH), 115.1 (C_q), 62.8 (CH_2), 50.4 (CH), 34.8 (CH_2), 34.2 (CH_2), 29.7 (CH), 25.6 (CH_3), 21.9 (CH_3), 14.3 (CH_3) ppm. MS (ESI+): m/z (%) = 300 (100) $[M + 1]^+$.

(±)-(*trans*)-Ethyl 3-Acetyl-2-methyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′d): Yellow oil. IR (neat): $\tilde{\nu}$ = 3074, 2952, 2934, 2874, 1734, 1702 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ = 8.56 (d, J = 8.2 Hz, 1 H), 7.43–7.34 (m, 3 H), 4.14 (q, J = 7.1 Hz, 2 H), 3.22 (dd, J = 4.9, 17.9 Hz, 1 H), 2.67 (m, 2 H), 2.57 (m, 1 H), 2.27 (ddd, J = 5.4, 9.9, 19.8 Hz, 1 H), 2.15 (m, 1 H), 1.92 (s, 3 H), 1.07 (t, J = 7.1 Hz, 3 H), 0.96 (d, J = 6.5 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, C_6D_6): δ = 208.8 (C_q), 150.9 (C_q), 135.6 (C_q), 133.7 (C_q), 129.0 (C_q), 123.2 (CH), 122.2 (CH), 117.0 (CH), 115.2 (CH), 114.3 (C_q), 61.6 (CH_2), 52.4 (CH), 32.5 (C_q), 30.7 (CH), 28.6 (CH_3), 23.1 (CH_2), 18.8 (CH_3), 13.2 (CH_3) ppm. MS (ESI+): m/z (%) = 300 (100) $[M + 1]^+$.

(±)-(*cis*)-Ethyl 3-Acetyl-2-methyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3d):[11a,25] Pink solid; m.p. 88.2 °C. IR (KBr): $\tilde{\nu}$ = 3034, 2914, 2873, 1727, 1706 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.6 Hz, 1 H), 7.46 (d, J = 6.9 Hz, 1 H), 7.32 (m, 2 H), 4.51 (q, J = 7.1 Hz, 2 H), 3.28 (m, 1 H), 3.07 (m, 1 H), 2.90 (m, 2 H), 2.79 (m, 2 H), 2.29 (s, 3 H), 1.51 (t, J = 7.1 Hz, 3 H), 0.94 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): 210.0 (C_q), 152.0 (C_q), 136.1 (C_q), 133.6 (C_q), 129.5 (C_q), 123.7 (CH), 122.8 (CH), 117.7 (CH), 115.5 (CH), 114.7 (C_q), 62.8 (CH_2), 50.7 (CH), 33.3 (CH_2), 29.3 (CH_3), 28.5 (CH), 18.3 (CH_2), 14.6 (CH_3), 14.4 (CH_3) ppm. MS [atmospheric pressure chemical ionization (APCI+)]: m/z (%) = 300 (100) $[M + 1]^+$.

Reactions of 1e and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.4 mg, 0.0067 mmol), AgOTf (1.7 mg, 0.0067 mmol), (*E*)-ethyl 2-(2-cyclohexylvinyl)-1*H*-indole-1-carboxylate (**1e**, 100 mg, 0.34 mmol), and 3-buten-2-one (**2a**, 28.3 mg, 0.41 mmol) at room temperature for 28 h. Purification of the residue (hexane/ethyl acetate, 99:1–98:2) progressively yielded **3′′b** (7 mg, 6%) and **3e** (92 mg, 74%). The same procedure was performed using $AuCl_3$ (2.0 mg, 0.0067 mmol) at room temperature for 3 h to yield **3′′b** (10 mg, 8%) and **3e** (109 mg, 87%).

Ethyl 4-Acetyl-2-cyclohexyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′′b): White solid; m.p. 87.5–88.6 °C. IR (KBr): $\tilde{\nu}$ = 3583, 3293, 2922, 1731, 1457, 1376, 1268, 1218, 1117, 746 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, major diastereomer): δ = 8.51 (d, J = 8.3 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 1 H), 7.37 (td, J = 1.1, 7.2 Hz, 1 H), 7.26 (m, 1 H), 4.15 (m, 2 H), 3.85 (m, 1 H), 3.18 (m, 1 H), 2.68 (m, 1 H), 2.02 (m, 1 H), 1.94 (s, 3 H), 1.85–1.67 (m, 5 H), 1.47–1.10 (m, 8 H), 1.07 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, C_6D_6, major diastereomer): δ = 208.0 (C_q), 150.9 (C_q), 136.9 (C_q), 135.8 (C_q), 128.2 (C_q), 123.3 (CH), 122.6 (CH), 117.7 (CH), 115.3 (CH), 114.3 (C_q), 61.7 (CH_2), 49.6 (CH), 41.8 (CH), 39.0 (CH), 29.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.5 (CH_2), 26.0 (CH_2), 24.5 (CH_3), 13.2 (CH_3) ppm. MS (ESI+): m/z (%) = 368 (100) $[M + 1]^+$, 390 (90) $[M + Na]^+$.

(±)-(*cis*)-Ethyl 3-Acetyl-2-cyclohexyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3e): White solid; m.p. 100.6–101.7 °C. IR (KBr): $\tilde{\nu}$ = 3400, 2924, 1730, 1456, 1347, 1327, 1210, 1144, 1042, 745 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ = 8.57 (d, J = 8.2 Hz, 1 H), 7.49 (d, J = 7.7 Hz, 1 H), 7.42 (td, J = 1.2, 7.2 Hz, 1 H), 7.36 (td, J = 1.0, 7.2 Hz, 1 H), 4.11 (m, 2 H), 3.52 (dd, J = 8.2, 18.0 Hz, 1 H), 3.28 (dd, J = 5.3, 18.0 Hz, 1 H), 2.97 (dd, J = 4.1, 16.6 Hz, 1 H), 2.85 (m, 1 H), 2.70 (dd, J = 6.2, 16.6 Hz, 1 H), 2.09 (d, J = 12.6 Hz, 1 H), 1.88 (m, 4 H), 1.82–1.68 (m, 5 H), 1.31–1.21 (m, 3 H), 1.04 (t, J = 7.7 Hz, 3 H), 0.97 (m, 2 H) ppm. ^{13}C NMR (125.75 MHz, C_6D_6): δ = 207.1 (C_q), 151.0 (C_q), 135.9 (C_q), 135.4 (C_q), 129.0 (C_q), 123.1 (CH), 122.1 (CH), 116.8 (CH), 115.4 (CH), 113.5 (C_q), 61.6 (CH_2), 48.8 (CH), 41.9 (CH), 40.7 (CH), 38.5 (CH_3), 31.5 (CH_2), 31.0 (CH_2), 27.5 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 13.1 (CH_3) ppm. MS (ESI+): m/z (%) = 368 (48) $[M + 1]^+$, 390 (100) $[M + Na]^+$. $C_{23}H_{29}NO_3$ (367.48): calcd. C 75.17, H 7.95, N 3.81; found C 75.08, H 7.91, N 3.82.

Reactions of 1f and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.7 mg, 0.0074 mmol), AgOTf (1.9 mg, 0.0074 mmol), (*E*)-ethyl 2-(hex-1-enyl)-1*H*-indole-1-carboxylate (**1f**, 100 mg, 0.37 mmol), and 3-buten-2-one (**2a**, 31.0 mg, 0.44 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 99:1–98:2) progressively yielded **3′′c** (13 mg, 10%) and **3f** (91 mg, 72%). The same procedure was performed using $AuCl_3$ (1.9 mg, 0.0064 mmol) at room temperature for 5 h to yield **3′′c** (10 mg, 7%), **3f** (70 mg, 55%).

Ethyl 4-Acetyl-2-*n*-butyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′′c):[11a,25] Yellow oil. IR (neat): $\tilde{\nu}$ = 2957, 2928, 2859, 1736 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ = 8.14 (d, J = 7.9 Hz, 1 H), 7.25 (m, 3 H), 4.51 (m, 2 H), 3.84 (m, 1 H), 3.32 (m, 1 H), 2.61 (m, 1 H), 2.21 (m, 1 H), 2.09 (s, 3 H), 1.81 (m, 1 H), 1.52 (t, J = 7.1 Hz, 3 H), 1.36–1.30 (m, 7 H), 0.95 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$, major diastereomer): δ = 211.5 (C_q), 152.3 (C_q), 137.9 (C_q), 136.4 (C_q), 128.8 (C_q), 124.3 (CH), 123.5 (CH), 118.5 (CH), 116.1 (CH), 115.1 (C_q), 63.4 (CH_2), 50.2 (CH), 36.6 (CH_2), 34.9 (CH), 33.5 (CH_2), 32.6 (CH_2), 29.5 (CH_2), 26.5 (CH_3), 23.3 (CH_2), 14.8 (CH_3), 14.5 (CH_3) ppm. MS (ESI+): m/z (%) = 364 (100) $[M + Na]^+$, 296 (40).

(±)-(*cis*)-Ethyl 3-Acetyl-2-*n*-butyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3f):[11a,25] Yellow oil. IR (neat): $\tilde{\nu}$ = 2955, 2926, 2870, 1735, 1707 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, J = 7.1 Hz, 1 H), 7.38 (m, 3 H), 4.52 (q, J = 7.1 Hz, 2 H), 3.19 (m, 2

H), 2.83 (m, 3 H), 2.48 (m, 1 H), 2.28 (s, 3 H), 1.49 (t, J = 7.1 Hz, 3 H), 1.25 (m, 6 H), 0.88 (m, 3 H) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): δ = 210.5 (C_q), 152.4 (C_q), 136.4 (C_q), 134.4 (C_q), 129.9 (C_q), 124.1 (CH), 123.2 (CH), 118.1 (CH), 115.9 (CH), 115.5 (C_q), 63.2 (CH_2), 51.4 (CH), 35.6 (CH), 30.7 (CH_2), 30.1 (CH_2), 29.1 (CH_3), 28.8 (CH_2), 23.2 (CH_2), 19.6 (CH_2), 14.8 (CH_3), 14.4 (CH_3) ppm. MS (ESI+): m/z (%) = 364 (100) $[M + Na]^+$.

Reactions of 1a and 2b with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.3 mg, 0.0066 mmol), AgOTf (1.7 mg, 0.0066 mmol), (*E*)-ethyl 2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1a**, 100 mg, 0.33 mmol), and (*E*)-4-phenylbut-3-en-2-one (**2b**, 58.0 mg, 0.40 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 95:5) progressively yielded **3′g** (65 mg, 43%) and **3g** (62 mg, 41%). The same procedure was performed using $AuCl_3$ (2.0 mg, 0.0066 mmol) at room temperature for 1.5 h to yield **3′g** (62 mg, 42%) and **3g** (65 mg, 44%).

(±)-(*trans*)-Ethyl 3-Acetyl-4-phenyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′g): White solid; m.p. 189.8–190.6 °C. IR (KBr): $\tilde{\nu}$ = 3437, 2927, 1728, 1705, 1343, 1043 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.4 Hz, 1 H), 7.35–7.10 (m, 10 H), 6.95 (t, J = 7.3 Hz, 1 H), 6.53 (d, J = 7.8 Hz, 1 H), 4.60–4.38 (m, 3 H), 3.55 (m, 1 H), 3.36 (m, 3 H), 2.35 (s, 3 H), 1.47 (t, J = 7.1 Hz, 3 H), 1.35 (s, 3 H) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): δ = 212.6 (C_q), 152.3 (C_q), 142.6 (C_q), 139.6 (C_q), 137.1 (C_q), 136.6 (C_q), 135.8 (C_q), 129.8 (CH), 129.2 (CH), 128.9 (C_q), 128.7 (CH), 128.2 (CH), 127.5 (CH), 124.0 (CH), 122.9 (CH), 120.2 (CH), 118.5 (C_q), 115.7 (CH), 63.4 (CH_2), 63.3 (CH), 45.7 (CH), 45.0 (CH), 34.11 (CH), 34.08 (CH_2), 21.4 (CH_3), 14.9 (CH_3) ppm. MS (ESI+): m/z (%) = 452 (20) $[M + 1]^+$, 474 (40) $[M + Na]^+$. $C_{30}H_{29}NO_3$ (451.56): calcd. C 79.80, H 6.47, N 3.10; found C 79.71, H 6.39, N 2.97.

(±)-(*cis*)-Ethyl 3-Acetyl-4-phenyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3g): White solid; m.p. 184.8–185.9 °C. IR (KBr): $\tilde{\nu}$ = 3437, 2920, 1731, 1703, 1376, 1051 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.4 Hz, 1 H), 7.27 (m, 6 H), 7.05 (m, 5 H), 6.85 (d, J = 7.8 Hz, 1 H), 4.53 (m, 3 H), 3.66 (d, J = 6.5 Hz, 2 H), 3.56 (m, 1 H), 3.36 (t, J = 4.2 Hz, 1 H), 2.32 (s, 3 H), 1.99 (s, 3 H), 1.53 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): δ = 208.9 (C_q), 152.4 (C_q), 143.6 (C_q), 139.2 (C_q), 136.9 (C_q), 136.8 (C_q), 136.5 (C_q), 129.6 (CH), 129.3 (C_q), 129.01 (CH), 128.98 (CH), 128.0 (CH), 127.2 (CH), 124.1 (CH), 123.1 (CH), 119.5 (CH), 117.2 (C_q), 115.9 (CH), 63.4 (CH_2), 61.2 (CH), 39.9 (CH), 39.1 (CH), 31.6 (CH), 29.8 (CH_2), 21.4 (CH_3), 14.8 (CH_3) ppm. MS (ESI+): m/z (%) = 452 (35) $[M + 1]^+$, 474 (100) $[M + Na]^+$. $C_{30}H_{29}NO_3$ (451.56): calcd. C 79.80, H 6.47, N 3.10; found C 79.77, H 6.43, N 2.03.

Reactions of 1e and 2b with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (2.1 mg, 0.0042 mmol), AgOTf (1.1 mg, 0.0042 mmol), (*E*)-ethyl 2-(2-cyclohexylvinyl)-1*H*-indole-1-carboxylate (**1e**, 62 mg, 0.21 mmol), and (*E*)-4-phenylbut-3-en-2-one (**2b**, 36.6 mg, 0.25 mmol) at room temperature for 48 h and then at 80 °C for 17 h. Purification of the residue (hexane/ethyl acetate, 97:3) progressively yielded **3′h** (24 mg, 26%) and **3h** (25 mg, 27%). The same procedure was performed using $AuCl_3$ (1.3 mg, 0.0042 mmol) at room temperature for 48 h and then at 80 °C for 17 h to yield progressively **1e** (31 mg, 50%), **3′h** (20 mg, 22%), and **3h** (15 mg, 16%).

(±)-(*trans*)-Ethyl 3-Acetyl-2-cyclohexyl-4-phenyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′h): Yellow solid; m.p. 145.8–147.0 °C. IR (KBr): $\tilde{\nu}$ = 3436, 2924, 1729, 1711, 1350, 1041 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 1 H), 7.33–7.10 (m, 6 H), 6.88 (t, J = 7.3 Hz, 1 H), 6.42 (d, J = 7.7 Hz, 1 H), 4.59–4.47 (m, 2 H), 4.22 (m, 1 H), 3.27 (ddd, J = 1.5, 5.5, 8.3 Hz, 1 H), 3.06–2.87 (m, 2 H), 2.24 (m, 1 H), 1.80–1.17 (m, 11 H), 1.76 (s, 3 H), 1.52 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 213.9 (C_q), 152.3 (C_q), 142.5 (C_q), 136.4 (C_q), 136.3 (C_q), 129.0 (CH), 128.8 (C_q), 128.5 (CH), 127.3 (CH), 123.6 (CH), 122.7 (CH), 119.9 (CH), 118.1 (C_q), 115.5 (CH), 63.1 (CH_2), 60.4 (CH), 46.2 (CH), 43.3 (CH), 40.0 (CH), 33.5 (CH_3), 32.3 (CH_2), 27.1 (CH_2), 27.0 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 25.8 (CH_2), 14.7 (CH_3) ppm. MS (ESI+): m/z (%) = 444 (100) $[M + 1]^+$. $C_{29}H_{33}NO_3$ (443.58): calcd. C 78.52, H 7.50, N 3.16; found C 78.48, H 7.42, N 3.05.

(±)-(*cis*)-Ethyl 3-Acetyl-2-cyclohexyl-4-phenyl-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3h): Yellow solid; m.p. 157.8–159.9 °C. IR (KBr): $\tilde{\nu}$ = 3443, 2930, 1733, 1706, 1374, 1047 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.4 Hz, 1 H), 7.22 (m, 5 H), 7.02 (m, 3 H), 4.52 (m, 3 H), 3.36 (dd, J = 6.2, 18.3 Hz, 1 H), 3.16 (m, 2 H), 2.28 (s, 3 H), 1.94 (m, 1 H), 1.80–0.70 (m, 11 H), 1.51 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 209.3 (C_q), 152.3 (C_q), 143.5 (C_q), 138.2 (C_q), 136.6 (C_q), 129.3 (C_q), 128.7 (CH), 128.3 (CH), 126.8 (CH), 123.9 (CH), 122.9 (CH), 118.4 (CH), 115.8 (CH), 115.2 (C_q), 63.1 (CH_2), 55.7 (CH), 40.2 (CH), 39.5 (CH), 38.0 (CH), 32.0 (CH_2), 31.4 (CH_2), 30.6 (CH_3), 28.0 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 14.7 (CH_3) ppm. MS (ESI+): m/z (%) = 444 (90) $[M + 1]^+$, 466 (100) $[M + Na]^+$. $C_{29}H_{33}NO_3$ (443.58): calcd. C 78.52, H 7.50, N 3.16; found C 78.43, H 7.46, N 3.12.

Reactions of 1a and 2c with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.3 mg, 0.0066 mmol), AgOTf (1.7 mg, 0.0066 mmol), (*E*)-ethyl 2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1a**, 100 mg, 0.33 mmol), and prop-2-enal (**2c**, 22.2 mg, 0.40 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 98:2–95:5) progressively yielded **3′i** (29 mg, 24%) and **3i** (78 mg, 65%). The same procedure was performed using $AuCl_3$ (2.0 mg, 0.0066 mmol) at room temperature for 1.5 h to yield **3′i** (22 mg, 18%) and **3i** (93 mg, 78%).

(±)-(*trans*)-Ethyl 3-Formyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′i): White oil. IR (neat): $\tilde{\nu}$ = 3436, 2916, 2725, 1728, 1619, 1457, 1376, 1398, 1212, 1142 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.62 (d, J = 2 Hz, 1 H), 8.19 (d, J = 8.1 Hz, 1 H), 7.47 (d, J = 7.1 Hz, 1 H), 7.35–7.27 (m, 2 H), 7.23–7.14 (m, 4 H), 4.48 (q, J = 7.1 Hz, 2 H), 3.52 (dd, J = 5.92, 18.1 Hz, 1 H), 3.44 (m, 1 H), 3.24 (m, 1 H), 3.10–2.97 (m, 2 H), 2.88 (m, 1 H), 2.37 (s, 3 H), 1.46 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 203.2 (CH), 151.2 (C_q), 138.7 (C_q), 136.0 (C_q), 135.3 (C_q), 133.6 (C_q), 128.9 (CH), 128.5 (C_q), 126.8 (CH), 123.4 (CH), 122.3 (CH), 117.1 (CH), 114.9 (CH), 114.0 (C_q), 62.3 (CH_2), 50.5 (CH), 40.6 (CH), 31.8 (CH_2), 20.3 (CH_3), 19.9 (CH_2), 13.7 (CH_3) ppm. MS (ESI+): m/z (%) = 362 (70) $[M + 1]^+$, 384.3 (75) $[M + Na]^+$. $C_{23}H_{23}NO_3$ (361.43): calcd. C 76.43, H 6.41, N 3.88; found C 76.38, H 6.37, N 3.91.

(±)-(*cis*)-Ethyl 3-Formyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3i): Yellow solid; m.p. 141.7–142.4 °C. IR (KBr): $\tilde{\nu}$ = 3430, 2916, 2690, 1727, 1614, 1378, 1336, 1206, 1035 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.85 (d, J = 0.8 Hz, 1 H), 8.20 (d, J = 8.1 Hz, 1 H), 7.49 (d, J = 7.2 Hz, 1 H), 7.36–7.29 (m, 2 H), 7.15–7.10 (m, 4 H), 4.52 (m, 2 H), 3.84 (m, 1 H), 3.63 (dd, J = 6.2, 18.4 Hz, 1 H), 3.52 (dd, J = 6.2, 18.4 Hz, 1 H), 3.10 (m, 1 H), 3.01 (dd, J = 5.4, 16.5 Hz, 1 H), 2.94 (dd, J = 7.2, 16.5 Hz, 1 H), 2.34 (s, 3 H), 1.51 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 202.7 (CH), 151.2 (C_q), 137.4

(C_q), 136.0 (C_q), 135.5 (C_q), 133.6 (C_q), 128.7 (CH), 128.5 (C_q), 127.0 (CH), 123.4 (CH), 122.3 (CH), 117.2 (CH), 114.9 (CH), 114.7 (C_q), 62.3 (CH_2), 49.9 (CH), 39.1 (CH), 29.5 (CH_2), 20.3 (CH_3), 18.8 (CH_2), 13.7 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 362 (60) $[M + 1]^+$. $C_{23}H_{23}NO_3$ (361.43): calcd. C 76.43, H 6.41, N 3.88; found C 76.41, H 6.40, N 3.90.

Reactions of 1a and 2d with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.3 mg, 0.0066 mmol), AgOTf (1.7 mg, 0.0066 mmol), (*E*)-ethyl 2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1a**, 100 mg, 0.33 mmol), and (*E*)-3-phenylprop-2-enal (**2d**, 52.3 mg, 0.40 mmol) at room temperature for 24 h. Purification of the residue (toluene/hexane, 90:10) progressively yielded **3′j** (45.5 mg, 32%) and **3j** (55.5 mg, 38%). The same procedure was performed using $AuCl_3$ (2.0 mg, 0.0066 mmol) at room temperature for 48 h to yield progressively **1a** (25 mg, 25%), **3′j** (30 mg, 21%), and **3j** (59 mg, 41%).

(±)-(*trans*)-Ethyl 3-Formyl-4-phenyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3′j):[11a] Yellow oil. IR (neat): ṽ = 2906, 2895, 2786, 1732 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 9.36 (d, *J* = 2.9 Hz, 1 H), 8.56 (m, 1 H), 6.94–7.33 (m, 12 H), 4.61 (m, 1 H), 4.10 (m, 2 H), 3.52 (ddd, *J* = 1.5, 5.0, 17.8 Hz, 1 H), 3.28 (m, 2 H), 3.11 (ddd, *J* = 5.0, 11.3, 11.4 Hz, 1 H), 2.20 (s, 3 H), 1.01 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, C_6D_6): δ = 202.7 (CH), 152.0 (C_q), 142.8 (C_q), 139.0 (C_q), 137.1 (C_q), 137.0 (C_q), 135.7 (C_q), 130.3 (CH), 129.4 (C_q), 129.3 (CH), 129.1 (CH), 128.1 (CH), 127.4 (CH), 124.3 (CH), 123.3 (CH), 120.5 (CH), 118.4 (C_q), 116.1 (CH), 63.0 (CH_2), 61.1 (CH), 44.1 (CH), 42.3 (CH), 35.2 (CH_2), 21.2 (CH_3), 14.3 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 460 (100) $[M + Na]^+$.

(±)-(*cis*)-Ethyl 3-Formyl-4-phenyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole-9(2*H*)-carboxylate (3j):[11a] Yellow oil. IR (neat): ṽ = 3027, 2924, 2853, 1734 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 9.74 (d, *J* = 1 Hz, 1 H), 8.56 (d, *J* = 8.3 Hz, 1 H), 6.97–7.35 (m, 12 H), 4.87 (d, *J* = 2.9 Hz, 1 H), 4.14 (m, 2 H), 3.67 (m, 2 H), 3.56 (m, 1 H), 3.07 (m, 1 H), 2.17 (s, 3 H), 1.06 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, C_6D_6): δ = 201.5 (CH), 152.0 (C_q), 143.2 (C_q), 139.0 (C_q), 137.2 (C_q), 136.6 (C_q), 136.5 (C_q), 129.7 (CH), 129.5 (C_q), 129.1 (CH), 129.0 (CH), 128.2 (CH), 127.2 (CH), 124.6 (CH), 123.5 (CH), 119.7 (CH), 117.1 (C_q), 116.3 (CH), 63.0 (CH_2), 60.3 (CH), 38.6 (CH), 37.4 (CH), 29.3 (CH_2), 21.1 (CH_3), 14.2 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 460 (100) $[M + Na]^+$.

Reactions of 1a and 2e with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.3 mg, 0.0066 mmol), AgOTf (1.7 mg, 0.0066 mmol), (*E*)-ethyl 2-(4-methylstyryl)-1*H*-indole-1-carboxylate (**1a**, 100 mg, 0.33 mmol), and 1-cyclopentencarbaldehyde (**2e**, 47.2 mg, 0.50 mmol) at room temperature for 12 h and at 110 °C for 12 h. Purification of the residue (toluene/hexane, 80:20) progressively yielded **1a** (18 mg, 18%), **3′k** (47 mg, 35%), and **3k** (61 mg, 46%). The same procedure was performed using $AuCl_3$ (2.0 mg, 0.0066 mmol) at room temperature for 24 h to yield progressively **1a** (50 mg, 50%), **3′k** (12 mg, 9%), and **3k** (20 mg, 15%).

(±)-(3a,4-*trans*)-Ethyl 3a-Formyl-4-(*p*-tolyl)-1,3,3a,4,5,10c-hexahydrocyclopenta[*c*]carbazole-6(2*H*)-carboxylate (3′k):[11b] Yellow oil. IR (neat): ṽ = 3047, 2934, 2871, 2693, 1728, 1612, 1513, 1458 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 9.46 (s, 1 H), 8.59 (d, *J* = 8.2 Hz, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.42 (m, 1 H), 7.34 (m, 1 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 3.56 (m, 1 H), 3.39 (m, 2 H), 3.22 (m, 1 H), 2.21 (s, 3 H), 2.17 (m, 1 H), 1.92 (m, 2 H), 1.84 (m, 1 H), 1.60 (m, 1 H), 1.47 (m, 1 H), 1.01 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, C_6D_6): δ = 203.8 (CH), 152.0 (C_q), 138.6 (C_q), 137.2 (C_q), 136.9 (C_q), 134.3 (C_q), 129.7 (CH), 129.5 (C_q), 128.8 (CH), 124.4 (CH), 123.3 (CH), 119.2 (CH), 118.7 (C_q), 116.4 (CH), 62.9 (CH_2), 62.4 (C_q), 44.4 (CH), 39.1 (CH), 30.1 (CH_2), 29.4 (CH_2), 24.5 (CH_2), 24.3 (CH_2), 21.1 (CH_3), 14.3 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 402 (100) $[M + 1]^+$. $C_{26}H_{27}NO_3$ (401.50): calcd. C 77.78, H 6.78, N 3.49; found C 77.75, H 6.69, N 3.43.

(±)-(3a,4-*cis*)-Ethyl 3a-Formyl-4-(*p*-tolyl)-1,3,3a,4,5,10c-hexahydrocyclopenta[*c*]carbazole-6(2*H*)-carboxylate (3k):[11b] Yellow solid; m.p. 130–131 °C. IR (KBr): ṽ = 3052, 2942, 2871, 2699, 1735, 1615, 1514, 1475 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 9.68 (s, 1 H), 8.60 (d, *J* = 8.1 Hz, 1 H), 7.51 (d, *J* = 7.5 Hz, 1 H), 7.43 (m, 1 H), 7.36 (m, 1 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 4.05 (q, *J* = 7.1 Hz, 2 H), 3.81 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.46 (m, 2 H), 3.08 (dd, *J* = 9.6, 5.5 Hz, 1 H), 2.35 (m, 1 H), 2.18 (s, 3 H), 1.96 (m, 1 H), 1.75 (m, 3 H), 1.58 (m, 1 H), 0.97 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75.45 MHz, C_6D_6): δ = 203.0 (CH), 152.0 (C_q), 139.1 (C_q), 137.2 (C_q), 136.8 (C_q), 134.5 (C_q), 129.9 (C_q), 129.7 (CH), 129.5 (CH), 124.5 (CH), 123.3 (CH), 119.0 (CH), 118.9 (C_q), 116.5 (CH), 62.8 (CH_2), 60.0 (C_q), 44.9 (CH), 39.3 (CH), 32.3 (CH_2), 31.2 (CH_2), 31.0 (CH_2), 24.0 (CH_2), 21.1 (CH_3), 14.2 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 402 (100) $[M + 1]^+$. $C_{26}H_{27}NO_3$ (401.50): calcd. C 77.78, H 6.78, N 3.49; found C 77.62, H 6.83, N 3.47.

Reactions of 4 and 2a with Gold(I) Complex and Gold(III) Chloride: The general procedure was followed using $AuPPh_3Cl$ (3.8 mg, 0.0076 mmol), AgOTf (2.0 mg, 0.0076 mmol), (*E*)-5-methoxy-2-(4-methylstyryl)benzofuran (**4**, 100 mg, 0.38 mmol), and **2a** (52.2 mg, 0.46 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 98:2–95:5) progressively yielded unreacted **4** (18 mg, 18%), **5′** (17 mg, 13%), and **5** (61 mg, 48%). The same procedure was performed using $AuCl_3$ (2.3 mg, 0.0076 mmol) at room temperature for 24 h to yield unreacted **4** (27 mg, 27%), **5′** (3 mg, 2%), and **5** (62 mg, 49%).

(±)-(*trans*)-8-Methoxy-2-acetyl-3-(*p*-tolyl)-1,2,3,4-tetrahydrodibenzo[*b*,*d*]furan (5′): Yellow solid; m.p. 134.7–135.1 °C. IR (KBr): ṽ = 3419, 2922, 1712, 1609, 1459, 1356, 1201, 1029, 834 cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ = 7.42 (d, *J* = 8.8 Hz, 1 H), 7.04 (m, 5 H), 6.98 (dd, *J* = 2.5, 8.8 Hz, 1 H), 3.64 (s, 3 H), 3.15 (ddd, *J* = 5.6, 10.3, 21.3 Hz, 1 H), 2.91 (dd, *J* = 5.6, 16.6 Hz, 1 H), 2.83–2.71 (m, 3 H), 2.57 (dd, *J* = 4.0, 14.0 Hz, 1 H), 2.21 (s, 3 H), 1.66 (s, 3 H) ppm. ^{13}C NMR (125.75 MHz, C_6D_6): δ = 207.9 (C_q), 155.7 (C_q), 152.9 (C_q), 149.3 (C_q), 139.3 (C_q), 135.5 (C_q), 128.7 (CH), 128.5 (C_q), 127.0 (CH), 110.9 (CH), 110.8 (CH), 110.7 (C_q), 101.3 (CH), 54.6 (CH_3), 52.2 (CH), 42.1 (CH), 30.8 (CH_2), 29.0 (CH_3), 23.1 (CH_2), 20.0 (CH_3) ppm. MS (ESI+): *m*/*z* (%) = 335 (100) $[M + 1]^+$, 357 (55) $[M + Na]^+$. $C_{22}H_{22}O_3$ (334.41): calcd. C 79.02, H 6.63; found C 78. 98, H 6.61.

(±)-(*cis*)-8-Methoxy-2-acetyl-3-(*p*-tolyl)-1,2,3,4-tetrahydrodibenzo[*b*,*d*]furan (5): Yellow solid; m.p. 137.1–138.4 °C. IR (KBr): ṽ = 3389, 2915, 1704, 1614, 1480, 1385, 1205, 1026, 803 cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ = 7.41 (d, *J* = 8.8 Hz, 1 H), 7.06 (m, 3 H), 6.97 (m, 3 H), 3.59 (s, 3 H), 3.46 (m, 1 H), 3.21 (m, 1 H), 3.03 (dd, *J* = 5.8, 16.4 Hz, 1 H), 2.90 (m, 1 H), 2.67 (m, 2 H), 2.14 (s, 3 H), 1.80 (s, 3 H) ppm. ^{13}C NMR (125.75 MHz, C_6D_6): δ = 206.1 (C_q), 155.7 (C_q), 153.3 (C_q), 149.6 (C_q), 137.7 (C_q), 135.6 (C_q), 128.5 (CH), 127.0 (CH), 111.4 (C_q), 111.1 (CH), 110.9 (CH), 101.2 (CH), 54.6 (CH_3), 50.9 (CH), 39.7 (CH), 28.3 (CH_2), 28.1 (CH_3), 20.0 (CH_3), 19.5 (CH_2) ppm (Note: a C_q signal was under the C_6D_6 residue signal.) MS (ESI+): *m*/*z* (%) = 335 (100) $[M + 1]^+$, 357 (70) $[M + Na]^+$. $C_{22}H_{22}O_3$ (334.41): calcd. C 79.02, H 6.63; found C 78.95, H 6.59.

Reactions of 1g and 2a with Gold(I) Complex, Gold(III) Chloride, and Boron Trifluoride–Diethyl Ether: The general procedure was followed using $AuPPh_3Cl$ (4.3 mg, 0.0086 mmol), AgOTf (2.2 mg, 0.0086 mmol), (*E*)-2-(4-methylstyryl)-1*H*-indole (**1g**, 100 mg, 0.43 mmol), and **2a** (36.0 mg, 0.51 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 95:5–92:8) progressively yielded unreacted **1g** (20 mg, 20%), **6a** (57 mg, 44%), and **3l** (23 mg, 18%). The same procedure was performed using $AuCl_3$ (2.6 mg, 0.0086 mmol) at room temperature for 24 h to yield progressively **6a** (76 mg, 58%) and **3l** (24 mg, 18%). The general procedure for the $BF_3{\cdot}OEt_2$-catalyzed reaction was followed using (*E*)-2-(4-methylstyryl)-1*H*-indole (**1g**, 100 mg, 0.43 mmol) and 3-buten-2-one (**2a**, 45.0 mg, 0.64 mmol) in toluene (2 mL). $BF_3{\cdot}OEt_2$ (8.5 mg, 0.06 mmol) was added at –20 °C, and the mixture was stirred at the same temperature for 2.5 h. Purification of the residue (hexane/ethyl acetate, 95:5) progressively yielded **6a** (14 mg, 11%) and **3l** (22 mg, 17%).

(*E*)-2-(4-Methylstyryl)-3-(3′-oxo-butyl)-1*H*-indole (6a): Yellow oil. IR (neat): $\tilde{\nu}$ = 3361, 2919, 1703, 1451, 1116 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.53 (d, J = 7.7 Hz, 1 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.34–7.01 (m, 6 H), 6.79 (d, J = 16.5 Hz, 1 H), 3.14 (t, J = 7.5 Hz, 2 H), 2.82 (t, J = 7.5 Hz, 2 H), 2.35 (s, 3 H), 2.13 (s, 3 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 208.7 (C_q), 137.9 (C_q), 136.8 (C_q), 134.5 (C_q), 132.8 (C_q), 129.7 (CH), 128.9 (C_q), 126.5 (CH), 126.4 (CH), 123.3 (CH), 119.9 (CH), 118.9 (CH), 116.2 (CH), 115.6 (C_q), 110.8 (CH), 44.8 (CH_2), 30.4 (CH_3), 21.5 (CH_3), 18.4 (CH_2) ppm. MS (ESI+): *m*/*z* (%) = 304 (100) $[M + 1]^+$. $C_{21}H_{21}NO$ (303.40): calcd. C 83.13, H 6.98, N 4.62; found C 83.08, H 6.95, N 4.63.

(±)-(*cis*)-3-Acetyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole (3l): Yellow oil. IR (neat): $\tilde{\nu}$ = 3392, 2912, 1699, 1154 cm^{-1}. ^1H NMR [400 MHz, [D$_6$]DMSO (dimethyl sulfoxide)]: δ = 10.75 (s, 1 H), 7.38 (d, J = 7.4 Hz, 1 H), 7.29 (d, J = 8.0 Hz, 1 H), 7.06–6.88 (m, 6 H), 3.81 (pseudo-q, 1 H), 3.36 (dd, J = 6.4, 16.8 Hz, 1 H), 3.25 (pseudo-q, 1 H), 3.00 (dd, J = 3.6, 16.8 Hz, 1 H), 2.81 (dd, J = 5.3, 16.0 Hz, 1 H), 2.66 (dd, J = 9.4, 16.0 Hz, 1 H), 2.21 (s, 3 H), 2.16 (s, 3 H) ppm. ^{13}C NMR (100.4 MHz, [D$_6$]DMSO): δ = 209.8 (C_q), 139.6 (C_q), 136.7 (C_q), 135.9 (C_q), 134.0 (C_q), 129.2 (CH), 127.9 (CH), 127.5 (C_q), 120.7 (CH), 118.7 (CH), 117.7 (CH), 111.2 (CH), 107.4 (C_q), 52.0 (CH), 39.7 (CH), 29.6 (CH_3), 29.1 (CH_2), 21.0 (CH_3), 20.0 (CH_2) ppm. MS (ESI+): *m*/*z* (%) = 304 (100) $[M + 1]^+$. $C_{21}H_{21}NO$ (303.40): calcd. C 83.13, H 6.98, N 4.62; found C 83.06, H 6.92, N 4.67.

Reactions of 1h and 2a with Gold(I) Complex, Gold(III) Chloride, and Boron Trifluoride–Diethyl Ether: The general procedure was followed using $AuPPh_3Cl$ (4.0 mg, 0.008 mmol), AgOTf (2.1 mg, 0.008 mmol), (*E*)-2-(4-methylstyryl)-1-methylindole (**1h**, 100 mg, 0.40 mmol), and **2a** (34.0 mg, 0.49 mmol) at room temperature for 24 h. Purification of the residue (hexane/ethyl acetate, 95:5–90:10) yielded **3m** (91 mg, 72%). The same procedure was performed using $AuCl_3$ (2.4 mg, 0.008 mmol) at room temperature for 24 h to yield progressively **1h** (14 mg, 14%), **6b** (73 mg, 57%), and **3m** (26 mg, 20%). The general procedure for the $BF_3{\cdot}OEt_2$-catalyzed reaction was followed using (*E*)-2-(4-methylstyryl)-1-methylindole (**1h**, 100 mg, 0.40 mmol) and **2a** (42.0 mg, 0.60 mmol) in toluene (2 mL). $BF_3{\cdot}OEt_2$ (8.5 mg, 0.06 mmol) was added at –20 °C, and the mixture was stirred at the same temperature for 4 h. Purification of the residue (hexane/ethyl acetate, 95:5) yielded **3m** (103 mg, 80%).

(*E*)-1-Methyl-2-(4-methylstyryl)-3-(3′-oxo-butyl)-1*H*-indole (6b): Yellow oil. IR (neat): $\tilde{\nu}$ = 3050, 3023, 2921, 1713, 1511, 1469, 1362, 1161 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.56 (m, 1 H), 7.44 (d, J = 8.1 Hz, 2 H), 7.32–7.03 (m, 6 H), 6.88 (d, J = 16.6 Hz, 1 H), 3.80 (s, 3 H), 3.18 (m, 2 H), 2.83 (m, 2 H), 2.39 (s, 3 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 208.8 (C_q), 138.1 (C_q), 138.0 (C_q), 134.8 (C_q), 134.7 (C_q), 132.6 (CH), 129.7 (CH), 127.8 (C_q), 126.53 (CH), 122.4 (CH), 119.5 (CH), 118.8 (CH), 116.7 (CH), 113.5 (C_q), 109.3 (CH), 44.7 (CH_2), 31.2 (CH_3), 30.3 (CH_3), 21.5 (CH_3), 19.4 (CH_2) ppm. MS (ESI+): *m*/*z* (%) = 318 (100) $[M + 1]^+$. $C_{22}H_{23}NO$ (317.42): calcd. C 83.24, H 7.30, N 4.41; found C 83.21, H 7.30, N 4.43.

(±)-(*cis*)-3-Acetyl-9-methyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-carbazole (3m): Yellow solid; m.p. 167.3–168.1 °C. IR (KBr): $\tilde{\nu}$ = 3048, 3023, 2908, 1698, 1514, 1472, 1349, 1161 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.7 Hz, 1 H), 7.35–6.95 (m, 7 H), 3.77 (m, 1 H), 3.66 (s, 3 H), 3.28–3.07 (m, 3 H), 2.96 (m, 2 H), 2.28 (s, 3 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 210.5 (C_q), 139.0 (C_q), 137.6 (C_q), 136.8 (C_q), 135.0 (C_q), 129.3 (CH), 128.0 (CH), 127.0 (C_q), 121.1 (CH), 119.1 (CH), 118.0 (CH), 108.9 (CH), 107.8 (C_q), 52.5 (CH), 41.0 (CH), 29.7 (CH_3), 29.4 (CH_3), 28.1 (CH_2), 21.2 (CH_3), 21.1 (CH_2) ppm. MS (ESI+): *m*/*z* (%) = 318 (100) $[M + 1]^+$. $C_{22}H_{23}NO$ (317.42): calcd. C 83.24, H 7.30, N 4.41; found C 83.19, H 7.27, N 4.46.

Reactions of 1j and 2a To Afford 1-Methyl-2-phenyl-3-(3′-oxobutyl)-1*H*-indole (6c): To a solution of $AuPPh_3Cl$ (3.76 mg, 0.0076 mmol) and AgOTf (1.95 mg, 0.0076 mmol) in toluene (1 mL) were added 1-methyl-2-phenyl-1*H*-indole (**1j**, 100 mg, 0.48 mmol) and **2a** (36.4 mg, 0.52 mmol). The solution was stirred at room temperature for 96 h. The solvent was then removed in vacuo, and the residue was purified by flash column chromatography over silica gel (hexane/ethyl acetate, 98:2–95:5) to yield **6c** (109 mg, 82%) as a yellow oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.67–7.13 (m, 9 H), 3.59 (s, 3 H), 3.02 (m, 2 H), 2.71 (m, 2 H), 2.07 (s, 3 H) ppm. ^{13}C NMR (50.4 MHz, $CDCl_3$): δ = 208.6 (C_q), 138.2 (C_q), 137.5 (C_q), 132.2 (C_q), 130.8 (CH), 128.7 (CH), 128.4 (CH), 127.6 (C_q), 122.0 (CH), 119.6 (CH), 119.0 (CH), 112.0 (C_q), 109.6 (CH), 45.1 (CH_2), 30.9 (CH_3), 30.0 (CH_3), 19.3 (CH_2) ppm. MS (ESI+): *m*/*z* (%) = 278 (20) $[M + 1]^+$, 300 (45) $[M + Na]^+$. $C_{19}H_{19}NO$ (277.36): calcd. C 82.28, H 6.90, N 5.05; found C 82.26, H 6.89, N 5.02.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra, 2D NMR experiments, and X-ray crystallographic data.

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