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Synthesis of Nitrogen Heterocycles via Pd-Catalyzed Cross-Coupling of *o*-Alkenyl Anilides with Vinylic Halides and Triflates

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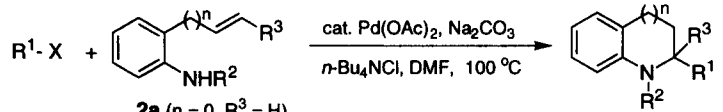
Abstract: The palladium-catalyzed cross-coupling of *o*-allylic and *o*-vinylic anilides with vinylic halides and triflates produces substituted nitrogen heterocycles in good to high yields by a process involving vinylpalladium addition to the olefin, rearrangement to a π-allylpalladium intermediate and subsequent intramolecular nucleophilic displacement of palladium. Different reactivity and regioselectivity in the palladium migration have been observed with different substituted alkenyl anilides.

Keywords: alkenyl halides, anilides, coupling reactions, palladium.

Since our initial report of the synthesis of unsaturated lactones via intermediate π-allylpalladium compounds derived from the cross coupling of vinylic mercurials and unsaturated carboxylic acids,[1] that methodology has been extended to vinylic halides and only catalytic amounts of palladium,[2] marking a significant step forward in widening the scope and the utility of this methodology as a general synthesis of heterocyclic compounds. Synthetic approaches to heterocycles as diverse as bicyclic nitrogen compounds,[3] pyrrolidines and piperidines,[4] dihydrobenzofurans and dihydrobenzopyrans[5] have since been reported. An important further extension of this chemistry would be to react *o*-alkenyl anilides with vinylic halides and triflates, in order to obtain substituted dihydroindoles and tetrahydroquinolines (eq. 1). We have therefore choosen to explore the reactions of vinylic halides and triflates with *o*-vinyl- and *o*-allylanilides. In examining more substituted analogues later on, questions regarding reactivity and the course and regiochemistry of the key rearrangement step leading to the π-allylpalladium complex have taken on major significance. Following our preliminary communications[6] on this work, in this paper we report the full details of our studies on this palladium-catalyzed cross-coupling process.



(1)

1

2a (n = 0, R^3 = H)
2b (n = 1, R^3 = H)
2c (n = 0, R^3 = Me)
2d (n = 1, R^3 = Me)

3

R^1 = vinylic; X = I, Br, O_3SCF_3; R^2 = H, Ts, $COCF_3$

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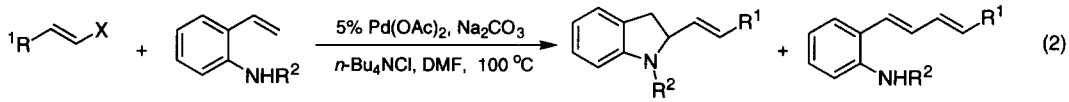
RESULTS AND DISCUSSION

Readily available *o*-vinyl- (**2a**) and *o*-allylanilides (**2b**) were selected as suitable starting materials for this chemistry. On the basis of our prior experience in the palladium-catalyzed cross-coupling of vinylic halides and triflates with *o*-alkenyl phenols,[5] we examined the same reaction conditions (5 mol % of $Pd(OAc)_2$, 1 equiv of the vinylic halide or triflate, 1.2 equiv of *o*-alkenyl anilide, 3.5 equiv of Na_2CO_3, 1.2 equiv of *n*-Bu_4NCl) used in that chemistry, selecting the cross-coupling of β-bromostyrene (**1**) and *o*-vinylaniline (**2a**) as our initial model system (eq. 2; R^1 = Ph, X = Br, R^2 = H).



(2)

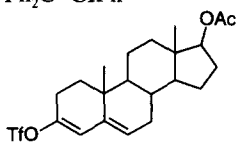
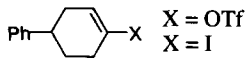
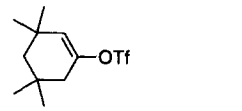
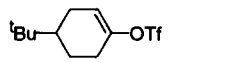
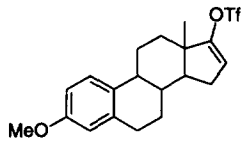
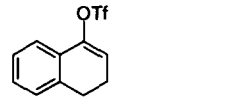
1 **2a** **3a** **4a**

The reaction proceeded as expected from our previous work and gave a moderate yield (45 %, 3 h) of the expected 2,3-dihydro-2-*(E)*-styrylindole (**3**) and only traces of the vinylic substitution product **4** (Table 1, entry 1). By employing the *N*-tosyl and *N*-trifluoroacetyl derivatives of **2a** instead, cleaner reactions and higher yields (68 and 75 % yields, respectively) were obtained (entries 2 and 3) . We also explored the effect on the reaction outcome of a variety of bases (Li_2CO_3, K_2CO_3, NaOAc, Et_3N), salts (LiCl), solvents (MeCN, DMSO, DMA) and temperatures (80, 120 °C), but no further improvement in the yield of **3** was obtained. We therefore applied our "optimal" reaction conditions to the synthesis of a variety of *N*-tosyl and *N*-trifluoroacetyl-2-vinylic dihydroindoles and tetrahydroquinolines and our results are summarized in Table 1 (entries 1-30).

Although the process is complicated by the competitive formation of vinylic substitution products, both *o*-vinyl and *o*-allyl-*N*-tosylanilides usually gave good yields of the expected heterocycle. However, while the cross-coupling of *N*-tosyl-*o*-vinylaniline with α- and β-bromostyrene gave quite good yields of the heterocycle (Table 1, entries 2 and 4), with other vinylic halides the vinylic substitution product often became the major product (entries 7, 9 and 11). In these cases, much more promising results were achieved by using the corresponding *N*-trifluoroacetanilide (entries 8, 10 and 12). Although formation of the diene was not completely suppressed with this substrate, the heterocycle was always the major product. On the other hand, *N*-tosyl-*o*-vinylaniline reacted reasonably efficiently with vinylic triflates to give the corresponding dihydroindoles in good yields, and the vinylic substitution products were observed as only minor products. A wide variety of vinylic iodides, bromides and triflates can be employed in this process and the yields are generally comparable. As predicted by the reaction mechanism (*vide infra*), both *(E)*- and *(Z)*-1-halo-1-alkenes gave exclusively the *(E)*-substituted product (compare entries 13 and 14). In general, the more hindered halides gave lower yields (see entries 16 and 30).

These reactions most likely proceed according to the mechanism outlined in Scheme 1 illustrated using a generic (*E*)-1-halo-1-alkene. The vinylic substrate oxidatively adds to Pd(0) produced by reduction of $Pd(OAc)_2$. The resulting vinylic palladium species apparently regioselectively adds to the carbon-carbon double bond of **2** to produce intermediate **5**. The high regioselectivity of this step may arise by prior coordination of either an anionic or neutral nitrogen moiety to the vinylpalladium intermediate. Subsequently, **5** undergoes

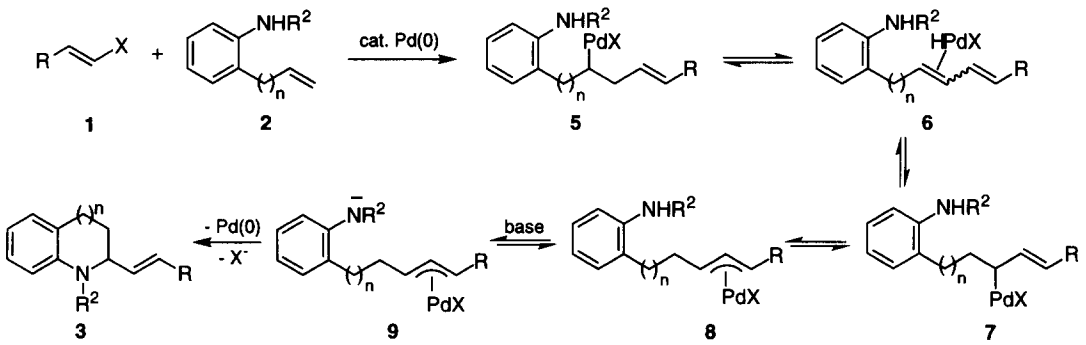
Table 1. Pd-Catalyzed Cross-Coupling of Vinylic Halides and Triflates (**1**) with Unsaturated Anilides (**2**).

Entry	Vinylic halide or triflate (**1**)	*o*-Alkenyl anilide (**2**)	R^2	Time (h)	**3** (%)[a]	**4** (%)[a]
1	*(E)*-PhCH=CHBr	*o*-$R^2NHC_6H_4CH=CH_2$ (**2a**)	H	3	45	trace
2			Ts	3	68	–
3			$COCF_3$	2	75	–
4	$PhCBr=CH_2$		Ts	3	59	–
5			$COCF_3$	4	64	–
6	*(E)*-*n*-BuCH=CHI		H	3	-	28
7			Ts	5	trace	63
8			$COCF_3$	2	39	42
9	*(E)*-MeCH=CBrMe		Ts	5	10	66
10			$COCF_3$	6	56	16
11	$Ph_2C=CHI$		Ts	2	12	70
12			$COCF_3$	2	71	13
13	*(E)*-*t*-BuCH=CHI			4	54	34
14	*(Z)*-*t*-BuCH=CHI			5	52	36
15	*(E)*-*cyclo*-$C_6H_{11}CH=CHI$			4	64	33
16	$Ph_2C=CIPh$			12	–	–
17			Ts	4	70	24
18	 X = OTf			1	61	35
19	X = I			3	46	39
20				3	65	33
21				3	65	33
22				7	47	–
23				3	52	40
24				2	87	7
25	*(E)*-PhCH=CHBr	*o*-$R^2NHC_6H_4CH_2CH=CH_2$ (**2b**)		24	80	–
26	*(E)*-*n*-BuCH=CHI			24	75	13[b]
27	*(E)*-*n*-BuCH=CHBr			24	70	4[b]
28	*(E)*-*t*-BuCH=CHBr			24	68	4[b]
29	*n*-$BuCI=CH_2$			24	47	5[b]
30	*(Z)*-EtCH=CIEt			24	28	3[b]
31	*(E)*-PhCH=CHBr	*(E)*-*o*-$R^2NHC_6H_4CH=CHCH_3$ (**2c**)		24	47	–
32		*(E)*-*o*-$R^2NHC_6H_4CH_2CH=CHCH_3$ (**2d**)		24	32	–
33	*(E)*-*t*-BuCH=CHBr			24	22	–

[a] Yields are calculated based on isolated compound. [b] Compound **4** was obtained as a mixture with **3** and the yield was determined by ^1H NMR spectral analysis.

regioselective palladium hydride elimination to generate intermediate **6**. In the allylanilide **2b**, the regioselectivity of this elimination may be a direct result of coordination of either an anionic or neutral nitrogen moiety to the palladium in **5**, thus preventing *syn* palladium hydride elimination towards the arene. Diene complex **6** can either undergo palladium hydride elimination to afford the observed diene side-product **4** or palladium hydride addition to the coordinated double bond with the opposite regiochemistry, which ultimately produces a σ-allylpalladium species, which rearranges to the key *syn*-π-allylpalladium intermediate that upon intramolecular nucleophilic displacement produces the desired nitrogen heterocycles bearing an *E*-double bond. The intermediacy of a π-allylpalladium species nicely explains the fact that both *(E)*- and *(Z)*-vinylic halides (entries 13 and 14) afford exclusively the *(E)*-configurated products. It is well known that *syn*-π-allylpalladium species are thermodynamically favored over their *anti*- counterparts[7] and are readily produced from σ-allylpalladium species containing a (*Z*)-double bond by a pi to sigma to pi interconversion.[8]

Scheme 1

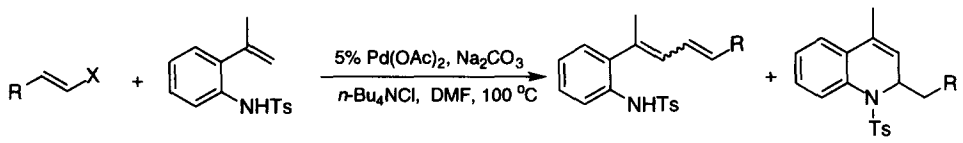


Our results suggest that the choice of the incoming nucleophile can be of considerable importance in achieving successful heterocyclization. Thus, *o*-vinylaniline itself failed to produce cyclic derivatives or gave only low yields of the desired *N*-heterocycle (see Table 1, entries 1 and 6). Much better results were obtained when using the corresponding tosylanilide. Even more significant is the change observed in the reactivity when introducing a trifluoroacetyl group. This provides evidence that the acidity of the nitrogen-hydrogen bond is an important feature of this heteroannulation process. The improved yields obtained using aniline derivatives bearing a strong electron-withdrawing group suggest that it is an anionic nitrogen species actually undergoing nucleophilic substitution of palladium, but we cannot rule out the possibility that the neutral nitrogen moiety is coordinating to palladium and then undergoing proton removal followed by substitution. Furthermore, vinylic triflates generally afford higher yields of the desired heterocycles (entries 17-24) suggesting that the nature of the counterion in the organopalladium intermediates plays a significant role. The ratio of heterocyclization to vinylic substitution obtained with 4-phenylcyclohexenyl triflate and the corresponding iodide supports this hypothesis (compare entries 18 and 19). It can be argued that the weakly coordinating triflate anion can be displaced from the coordination sphere of the metal by the nitrogen moiety in intermediate **6**. This intramolecular coordination would be expected to render the η^2-diene complex (**6**) less prone to undergo the irreversible elimination of palladium hydride leading to diene side-product and thus favor readdition of the hydride to the carbon-carbon

bond leading to the formation of **7**. The presence of the better leaving group triflate should also favor intramolecular nucleophilic substitution in the π-allylpalladium intermediate **9**.

We decided next to investigate whether alkyl-substituted olefinic tosylanilides would undergo intermolecular coupling with our vinylic halides and triflates to produce the corresponding more substituted heterocycles. The methyl substituted precursors, *o*-1-*(E)*-propenyl- (**2c**), *o*-crotyl- (**2d**), *o*-isopropenyl- (**2e**) and *o*-methallyl-*N*-tosylaniline (**2f**), all easily prepared by conventional chemistry, were subjected to our standard reaction conditions. The reactions of **2c** and **2d** with β-bromostyrene proceeded smoothly to give the expected heterocycles, albeit in relatively low yields (Table 1, entries 31 and 32). Unfortunately, with other vinylic halides and these two substrates, the reaction mixtures became more complicated, limiting the synthetic utility of this process.

Surprisingly, the reactions of vinylic halides with *o*-isopropenyl-*N*-tosylaniline (**2e**), containing a terminal α,α-disubstituted double bond, gave very unusual results (eq. 3), since the products formed were not the ones that would be expected on the basis of our previous experience and the above mechanism.



1 **2e** **10** **11** (3)

Exposure of *o*-isopropenyl-*N*-tosylaniline (**2e**) to β-bromostyrene (eq. 3, R = Ph, X = Br) under our usual reaction conditions resulted after 1 hour in the formation of the diene (**10**) in 40 % yield (as an 88:12 *Z/E* mixture), 2-benzyl-2,3-dihydro-4-methyl-*N*-tosylquinoline (**11**) in 7 % yield and **2e** was recovered in 15 % yield. Extending the reaction time to 24 hours, the composition of the mixture significantly changed, with the heterocycle **11** now being the major product (40 % yield) together with minor amounts of the diene **10** (15 % yield). Changing the reaction conditions by using different bases, salts, solvents and catalysts led to only a minor yield of **11**. Since TLC and GC analysis of the reaction mixture suggested that the heterocycle was derived from the diene, we decided to investigate the cyclization step separately, in order to develop a better understanding of the above results.

The data reported in Table 2 show that not only the presence of palladium is essential for the cyclization, but certain types of vinylic halides are also required. Virtually no reaction was observed when the Pd catalyst was omitted (entry 1), but little or no cyclization product was discernible even in the presence of different palladium catalysts (Table 2, entries 2-6). Both Pd(II) and Pd(0) catalysts were tested in basic, neutral and acidic reaction media, but with no significant cyclization observed. However, in the presence of both 5 mol % of $Pd(OAc)_2$ and 1 equiv of β-bromostyrene, diene **10** (R = Ph) was found to undergo a rapid (4 h) conversion into **11** in 63 % yield (Table 2, entry 7). We set out to explore the role of the organic halide in the process by examining the effect of different types of organic halides. The reactivity observed with *(E)*-1-iodo-1-hexene was comparable to that of β-bromostyrene, whereas PhI and 1-bromo-2-methylpropene were completely ineffective (Table 2, entries 8-10).

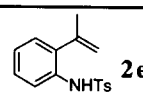
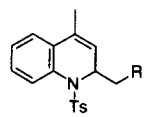
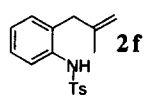
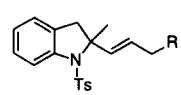
Table 2. Cyclization of Diene **10** (R = Ph).

Entry	Reaction Conditions [a]	**11** Yield % [b]
1	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv)	- (84)
2	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv), $Pd(OAc)_2$ (0.05 equiv)	- (88)
3	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv), $Pd(dba)_2$ (0.05 equiv)	20 (76)
4	$PdCl_2$ (0.05 equiv), MeCN (2 mL)	- (98)
5	TsOH (0.05 equiv), $Pd(dba)_2$ (0.05 equiv)	- (90)
6	$(Et_3NH)I$ (0.05), $Pd(PPh_3)_4$	- (93)
7	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv), $Pd(OAc)_2$ (0.05 equiv), *(E)*-PhCH=CHBr (1 equiv), 4 h	63
8	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv), $Pd(OAc)_2$ (0.05 equiv), *(E)*-*n*-BuCH=CHI (1 equiv), 4 h	74
9	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv), $Pd(OAc)_2$ (0.05 equiv), PhI (1 equiv)	-
10	Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.2 equiv), $Pd(OAc)_2$ (0.05 equiv), Me_2C=CHBr (1 equiv)	- (94)

[a] Unless otherwise stated, all reactions were carried out on a 0.25 mmol scale under an argon atmosphere in 2 mL of DMF for 24 h. [b] The number in parentheses refers to the yield of recovered starting material **10**.

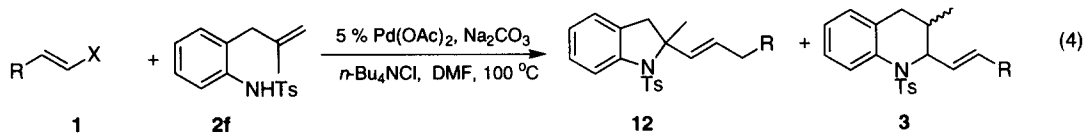
From a synthetic point of view, we reasoned that employing 2 equiv of β-bromostyrene in the reaction with *o*-isopropenyl-*N*-tosylaniline (**2e**) and allowing the reaction to proceed until disappearance of the diene **10**, should improve the yield of the heterocycle. In fact, this experiment led to the isolation of *N*-tosyl-2-benzyl-1,2-dihydro-4-methylquinoline (**11**) in 53 % yield after 6 h. The same protocol involving the use of 2 equiv of the vinylic halide worked well for the synthesis of a variety of substituted dihydroquinolines and our preparative results are reported in Table 3 (entries 1-7).

Table 3. Pd-Catalyzed Coupling of *o*-Isopropenyl and *o*-Methallyl Anilides with Vinylic Halides.[a]

Entry	Vinylic Halide (**1**)	Tosylanilide	Product	R	Time (h)	% Yield [b]
1	*(E)*-PhCH=CHBr	 **2e**	 **11**	Ph	8	59
2	*(E)*-*n*-BuCH=CHI			*n*-Bu	6	75 (72)[c]
3	*(E)*-*t*-BuCH=CHI			*t*-Bu	6	74 (67)[c]
4	*(E)*-*cyclo*-C_6H_{11}CH=CHI			*c*-C_6H_{11}	6	73
5	*(E)*-MeO_2CCH=CHI			MeO_2C	3	37
6	*(E)*-$PhCH_2$CH=CHI			$PhCH_2$	5	70
7	$PhCBr=CH_2$			-	-	-
8	*(E)*-*n*-BuCH=CHI	 **2f**	 **12**	*n*-Bu	6	59 (31)[c]
9	*(E)*-*n*-BuCH=CHBr				24	53 (13)[d]
10	*(E)*-PhCH=CHBr			Ph	10	62 (21)[d]
11	*(E)*-*t*-BuCHCH-Br			*t*-Bu	24	52 (27)[d]
12	Me_2C=CHX X = I			*i*-Pr	3	61[e]
13	X = Br				5	60[e]
14	X = OTf				2	32[e]
15	*(E)*-*cyclo*-C_6H_{11}CH=CHI			*c*-C_6H_{11}	6	66
16	*(E)*-$PhCH_2$CH=CHI			$PhCH_2$	6	31

[a] Unless otherwise stated, all reactions were carried out under an argon atmosphere on a 0.3-0.5 mmol scale in DMF as the solvent (3 mL) at 100 °C using the following molar ratios: **1**: **2**: Na_2CO_3: *n*-Bu_4NCl: $Pd(OAc)_2$ = 2 : 1 : 3.5 : 1.2 : 0.05. [b] Yields are calculated based on pure, isolated compound, fully characterized by ^1H and ^{13}C NMR, IR and mass spectral analysis. [c] The number in parentheses refers to the yield of heterocycle when only 1 equiv of vinylic halide was used. [d] The number in parentheses refers to the yield of the corresponding 3-methyl-2-vinyltetrahydroquinolines. [e] Only 1 equiv of vinylic halide was used.

The reactions of *o*-methallyl-*N*-tosylaniline (**2f**) with different vinylic halides also gave the unexpected product 2-alkenyl-2-methyldihydroindole (**12**) as the major product (eq. 4). Since analysis of many of the reaction mixtures obtained suggested a similar two-step mechanism involving diene intermediates in the heterocycle-forming reaction path, the same protocol developed earlier for the reactions of *o*-isopropenyl-*N*-tosylaniline (**2e**) was applied to **2f**. These experiments usually gave satisfactory preparative results (Table 3, entries 8-16). However, with this substrate, minor amounts of the 3-methyl-2-vinyltetrahydroquinoline **3**, undoubtedly arising by the mechanism reported in Scheme 1 for the unsubstituted *o*-vinyl- and *o*-allylanilides, were sometimes isolated (Table 3, entries 8-11). In some cases, both with *o*-isopropenyl- and *o*-methallyl-*N*-

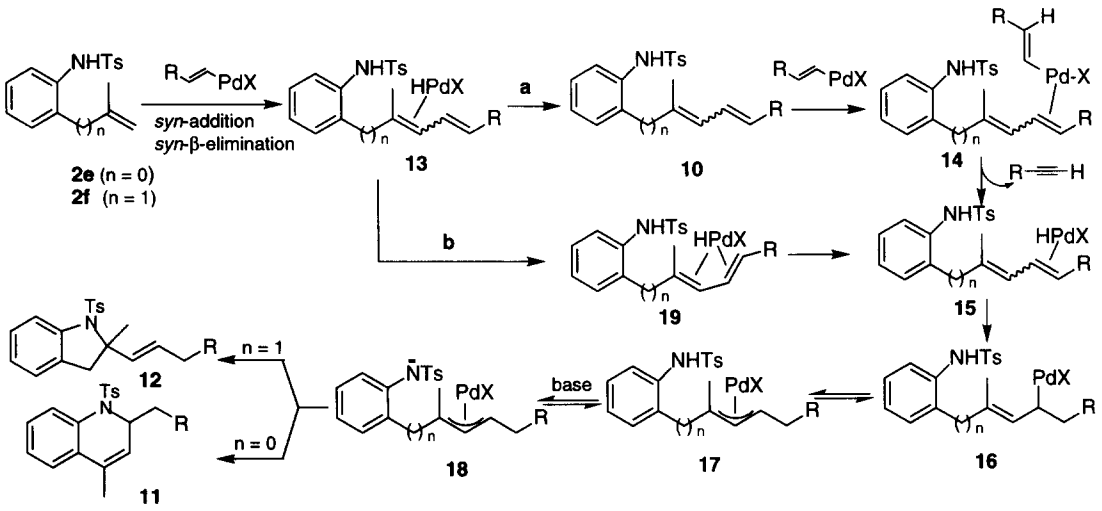


(4)

tosylaniline, the utilization of two equivalents of the vinylic halide appeared not to be crucial for the success of the reaction (see for example entries 2, 3 and 12-14), but no attempts have been made to optimize the ratio for any particular example.

Mechanistically, the two reaction paths illustrated in Scheme 2 are consistent with our experimental evidence.

Scheme 2



The initial steps leading to the η^2-diene complex **13** are common to the previously reported reactions. Apparently, the substitution pattern present in **13** can either alter the regiochemistry of the palladium hydride readdition or affect the cyclization by an entirely different mechanism, involving prior formation of the free diene **10**, observed in many of these reactions as an intermediate. The central question is how the complexed diene **13** reacts to give the observed product. According to path a, the free diene is first formed, but then reacts further with a second equivalent of the σ-vinylpalladium complex to coordinate the less hindered double bond. This intermediate (**14**) then undergoes a palladium hydride elimination to give the η^2-complexed diene **15**.

Subsequent π-allylpalladium formation and intramolecular displacement afford the observed product. According to this pathway, the second equivalent of vinylic halide is required as the source of palladium hydride. This hypothesis is supported by the fact that no cyclization product was observed when **10** (R = Ph) was reacted with 1-bromo-1-methylpropene or phenyl iodide under the usual reaction conditions, while both *(E)*-1-iodo-1-hexene and β-bromostyrene afforded cyclized product. However, other catalytic precursors reported to generate hydridopalladium species, which were tested in order to find conditions for cyclization not requiring an excess of the vinylic halide, were not satisfactory in the present system (see Table 2, entries 5[9] and 6[10]). Nevertheless, the successful cyclization of **2f** by reaction with 1 equiv of 1-halo-2-methylpropene (Table 3, entries 12-14), a vinylic halide unable to generate a Pd-H species in the suggested manner, clearly shows that a different pathway (Scheme 2, path b), not involving the intermediacy of free diene **10**, must be operating as well. Path b differs from path a in the way **15** is generated from **13**. It entails coordination of the second double bond of the diene being faster than the elimination of HPdX. Complex **15** is presumably generated through a bidentate diene complex **19**, as suggested previously by Heck.[11] The rather similar result obtained in the annulation of **2e** with either 1 or 2 equiv of *(E)*-1-iodo-1-hexene or *(E)*-1-iodo-4,4-dimethyl-1-butene also supports the idea that path b must be involved in many of these reactions.

In conclusion, the results reported here suggest the vast synthetic potential of this type of palladium catalyzed cross-coupling for the synthesis of substituted heterocycles. In this particular paper, we have been able to prepare a range of dihydroindoles and dihydroquinolines by the simple cross-coupling of unsaturated anilides and vinylic halides or triflates. Furthermore, the discovery of the unanticipated rearrangement observed with the *o*-isopropenyl- and *o*-methallylanilides further expands the scope of this palladium-catalyzed process. The unique features associated with these substrates provide a strong stimulus for further investigation into the effect of structure on these rearrangements. This should facilitate the logical design of analogous palladium-catalyzed cross-coupling processes based on this reaction principle.

EXPERIMENTAL SECTION

General. Melting points were obtained on a Thomas-Hoover or Büchi apparatus in open capillary tubes and are uncorrected. Proton and carbon NMR spectra were recorded on a Nicolet NT-300 (at 300 MHz and 75.5 MHz, respectively) or on a Bruker AC 200 (at 200 MHz and 50.3 MHz, respectively), using TMS as an internal standard. Infrared spectra were recorded with a Nicolet 5DX FT/IR or with a Beckman 4250 spectrometer. MS spectra were recorded with a Hewlett Packard HP 5980A spectrometer equipped with a Data System 5934A. High resolution mass spectral analyses were performed on a Kratos MS-50 spectrometer. Reaction products were purified on axially compressed columns, packed with 25-40μ SiO_2 (Macherey Nagel), connected to a Gilson solvent delivery system and a Gilson refractive index detector, or by flash column chromatography with 40-63μ SiO_2 (Merck).

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Palladium acetate was donated by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. All vinylic halides[12] and triflates[13] were synthesized by literature procedures. 2-Vinylaniline[14] (**2a**) was obtained from 2-aminobenzaldehyde according to a literature procedure.[15] *N*-Trifluoroacetyl-2-vinylaniline[16] was obtained in quantitative yield by reacting 2-vinylaniline with 2 equiv of trifluoroacetic anhydride in THF at 0 °C. *N*-Tosyl-2-

vinylaniline[17] and *N*-tosyl-2-[*(E)*-1-propenyl]-aniline[18] (**2c**) were obtained from 2-(*N*-tosylamino)benzaldehyde according to the procedure given in reference 13. 2-Aminobenzaldehyde (mp 36 °C; lit.[19] mp 36-7 °C) has been prepared in 70% yield by reacting the commercially available 2-aminobenzyl alcohol with MnO_2 in CH_2Cl_2. 2-(*N*-Tosylamino)benzaldehyde[20] has been obtained in 91 % yield from the oxidation of 2-(*N*-tosylamino)benzyl alcohol with PCC in CH_2Cl_2 in analogy to a published method.[21] *N*-Tosyl-2-isopropenylaniline (**2e**) was obtained from commercial 2-isopropenylaniline according to conventional chemistry. The structure of all these compounds were supported by satisfactory spectral data.

Preparation of *N*-Tosyl-2-allylanilines (2b, 2d, 2f). The *N*-tosyl-2-allylanilines were prepared by the reaction of *N*-tosyl-2-(iodomethyl)aniline and the corresponding vinylic magnesium bromide. *N*-Tosyl-2-(iodomethyl)aniline was prepared from 2-(*N*-tosylamino)benzyl alcohol and sodium iodide according to the procedure given in reference 20. In an oven dried, 50 mL round bottom flask equipped with a condenser and a stirring bar were placed magnesium turnings (9 mmol) and THF (3 mL) under a nitrogen atmosphere. A solution of the appropriate vinylic bromide (9 mmol) in 1 mL of THF was introduced slowly into the flask at room temperature with good stirring. After the formation of the Grignard reagent (about 30 min) a solution of *N*-tosyl-2-(iodomethyl)aniline (3 mmol) in THF (5 mL) was added slowly at room temperature and the mixture was stirred for 1 hour. The excess Grignard reagent was destroyed by adding water and the crude product was extracted with ethyl ether (100 mL). The ether solution was then dried over $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by flash column chromatography using 5:1 hexane/THF.

***N*-Tosyl-2-allylaniline (2b).** Obtained in 55 % isolated yield from the reaction of vinylmagnesium bromide and *N*-tosyl-2-(iodomethyl)aniline: mp 69-70 °C (lit.[18] 70.5-71 °C); ^{1}H NMR ($CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2 H), 7.40 (d, *J* = 7.8 Hz, 1 H), 7.23-7.04 (m, 5 H), 6.49 (s, 1 H), 5.78 (ddt, *J* = 17.1, 10.2, 5.7 Hz, 1 H), 5.11 (dd, *J* = 9.9, 1.5 Hz, 1 H), 4.94 (dd, *J* = 17.4, 1.5 Hz, 1 H), 3.01 (d, *J* = 5.7 Hz , 2 H), 2.39 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.8, 136.7, 135.6, 134.9, 132.1, 130.5, 129.6, 127.7, 127.1, 126.3, 124.5, 117.0, 36.2, 21.6; IR ($CDCl_3$) 3285, 1599, 1163 cm^{-1}.

***N*-Tosyl-2-crotylaniline (2d).** Obtained as a 56:44 *Z/E* mixture in 52 % isolated yield from the reaction of propenylmagnesium bromide and *N*-tosyl-2-(iodomethyl)aniline. *Z* isomer : ^{1}H NMR ($CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.28-7.00 (m, 5 H), 6.48 (s, 1 H), 5.73-5.60 (m, 1 H), 5.30-5.20 (m, 1 H), 3.02 (d, *J* = 6.9 Hz, 2 H), 2.39 (s, 3 H), 1.70 (d, *J* = 6.9 Hz, 3 H). *E* isomer: ^{1}H NMR same as the *Z* isomer or not seen, except δ 6.60 (s, 1 H), 5.41-5.35 (m, 2 H), 2.91 (br s, 2 H), 1.68-1.65 (m, 3 H). ^{13}C NMR ($CDCl_3$) of mixture δ 143.6, 136.6, 134.9, 134.7, 133.3, 132.9, 130.1, 129.7, 129.4, 128.2, 127.4, 127.2, 127.0, 126.9, 126.4, 126.1, 125.9, 124.3, 124.1, 34.8, 29.3, 21.4, 17.7, 12.7 (several peaks are not seen due to overlap); IR ($CDCl_3$) 3301, 1599, 1164 cm^{-1}.

***N*-Tosyl-2-methallylaniline (2f).** Obtained in 62 % isolated yield from the reaction of isopropenylmagnesium bromide and *N*-tosyl-2-(iodomethyl)aniline: mp 51-2 °C; ^{1}H NMR ($CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2 H), 7.46 (d, *J* = 8.1 Hz, 1 H), 7.24-7.18 (m, 3 H), 7.09 (dt, *J* = 7.2, 0.9 Hz, 1 H), 7.03 (dd, *J* = 7.5, 1.5 Hz, 1 H), 6.67 (s, 1 H), 4.89 (s, 1 H), 4.61 (s, 1 H), 2.91 (s, 2 H), 2.39 (s, 3 H), 1.57 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.8, 143.6, 136.9, 135.5, 131.3, 131.0, 129.6, 127.8, 127.1, 125.9, 124.1, 112.9, 41.0, 22.2, 21.6; IR ($CDCl_3$) 3308, 1599, 1164 cm^{-1}.

General Procedure for the Synthesis of 1,2-Dihydro-2-vinylindoles and 1,2,3,4-Tetrahydro-2-vinylquinolines (3). To a mixture of 5 mol % of $Pd(OAc)_2$ (0.03 mmol), 1.2 equiv of the

olefinic aniline (0.72 mmol), 3.5 equiv of Na_2CO_3, 1.2 equiv of *n*-Bu_4NCl in DMF (2 mL) was added 1.0 equiv of the vinylic halide (0.6 mmol) under an argon atmosphere. The reaction mixture was stirred at 100 °C for an appropriate time interval. The mixture was then diluted with Et_2O and washed with saturated NH_4Cl, followed by water. The organic layer was dried over $MgSO_4$, filtered, concentrated and purified by chromatography (silica gel, hexane/ethyl acetate as eluents). All reactions were carried out on the same scale in analogy to the foregoing procedure. The vinylic substitution by-product, when obtained, was usually isolated in the same manner and fully characterized. The reaction time and the yields are given in Table 1.

2,3-Dihydro-2-[*(E)*-β-styryl]indole (Table 1, entry 1): oil; IR (liquid film) 3365, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45-7.22 (m, 5 H), 7.12 (d, *J* = 7.8 Hz, 1 H), 7.06 (dt, *J* = 0.9, 7.5 Hz, 1 H), 7.43 (dt, *J* = 1.2, 7.5 Hz, 1 H), 6.70 (d, *J* = 7.8 Hz, 1 H), 6.60 (d, *J* = 15.6 Hz, 1 H), 6.37 (dd, *J* = 7.8, 15.6 Hz, 1 H), 4.52 (q, *J* = 8.1 Hz, 1 H), 3.28 (dd, *J* = 8.5, 15.6 Hz, 1 H), 2.90 (dd, *J* = 7.8, 15.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 150.6, 136.8, 131.6, 130.6, 128.7, 128.5, 127.7, 127.5, 126.5, 124.8, 118.9, 109.3, 62.4, 39.9; MS *m/z* (relative intensity) 221 (M^+, 100); HRMS *m/z* 221.1208 (calcd. 221.1204 for $C_{16}H_{15}N$).

***N*-Tosyl-2,3-dihydro-2-[*(E)*-β-styryl]indole (Table 1, entry 2)**: oil; IR (liquid film) 1599, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1 H), 7.61 (d, *J* = 8.1 Hz, 2 H), 7.35-7.20 (m, 6 H), 7.15 (d, *J* = 8.1 Hz, 2 H), 7.09-6.99 (m, 2 H), 6.68 (d, *J* = 15.6 Hz, 1 H), 6.15 (dd, *J* = 15.6, 6.9 Hz, 1 H), 5.05-4.86 (m, 1 H), 3.08 (dd, *J* = 15.9, 12.6 Hz, 1 H), 2.73 (dd, *J* = 15.9, 2.7 Hz, 1 H), 2.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.8, 141.4, 136.3, 135.7, 131.2, 129.5, 128.7, 128.4, 127.9, 127.8, 127.2, 126.6, 125.2, 124.4, 116.6, 63.9, 35.5, 21.5 (one signal is not seen due to overlap); HRMS *m/z* 375.1301 (calcd. 375.1293 for $C_{23}H_{21}NO_2$).

***N*-Trifluoroacetyl-2,3-dihydro-2-[*(E)*-β-styryl]indole (Table 1, entry 3)**: oil; IR (liquid film) 1683, 843, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1 H), 7.35-7.18 (m, 8 H), 6.50 (d, *J* = 16.0 Hz, 1 H), 6.20 (dd, *J* = 6.9, 16.0 Hz, 1 H), 5.37 (t, *J* = 7.6 Hz, 1 H), 3.63 (dd, *J* = 8.4, 15.7 Hz, 1 H), 3.00 (d, *J* = 15.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.5 (q, *J* = 37 Hz, $\underline{C}OCF_3$), 141.1, 135.9, 131.1, 130.7, 128.7, 128.2, 128.0, 127.6, 126.6, 126.3, 125.3, 118.8, 116.2 (q, *J* = 286 Hz, CF_3), 62.0, 36.8; MS *m/z* (relative intensity) 317 (M^+, 100), 220 (18); HRMS 317.1025 *m/z* (calcd. 317.1027 for $C_{18}H_{14}F_3NO$).

***N*-Tosyl-2,3-dihydro-2-(1-phenylethenyl)indole (Table 1, entry 4)**: oil; IR (liquid film) 1599, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1 H), 7.61 (d, *J* = 8.1 Hz, 2 H), 7.41-7.19 (m, 8 H), 7.03-6.98 (m, 2 H), 5.55 (d, *J* = 0.9 Hz, 1 H), 5.40 (s, 1 H), 5.30 (m, 1 H), 2.95 (dd, *J* = 15.8, 12.6 Hz, 1 H), 2.60 (dd, *J* = 15.8, 2.7 Hz, 1 H), 2.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.6, 144.1, 141.9, 138.9, 135.3, 131.4, 129.8, 128.6, 128.0, 127.9, 127.9, 127.0, 125.4, 124.9, 117.1, 113.7, 64.3, 35.7, 21.7; MS *m/z* (relative intensity) 375 (M^+, 100), 272 (36); HRMS *m/z* 375.1304 (calcd. 375.1293 for $C_{23}H_{21}NO_2S$).

***N*-Trifluoroacetyl-2,3-dihydro-2-(1-phenylethenyl)indole (Table 1, entry 5)**: mp 79-80 °C; IR (KBr) 1684, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1 H), 7.43-7.16 (m, 8 H), 5.69 (d, *J* = 9.3 Hz, 1 H), 5.27 (s, 1 H), 4.94 (s, 1 H), 3.54 (dd, *J* = 9.3, 15.8 Hz, 1 H), 2.89 (d, *J* = 15.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.3 (q, *J* = 37 Hz, $\underline{C}OCF_3$), 147.5, 142.0, 138.0, 130.2, 128.9, 128.5, 128.0, 126.7, 126.2, 125.5, 118.3, 117.0 (q, *J* = 286 Hz, CF_3), 111.8, 62.0, 36.3; MS *m/z* (relative intensity) 317 (M^+, 65), 117 (100); HRMS *m/z* 317.1022 (calcd. 317.1027 for $C_{18}H_{14}F_3NO$).

2-[*(E)*-1,3-Octadienyl]aniline (Table 1, entry 6): oil; IR ($CDCl_3$) 3456, 3376, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (dd, *J* = 10.8, 1.2 Hz, 1 H), 7.06 (dt, *J* = 6.0, 1.8 Hz, 1 H), 6.78-6.60 (m, 3 H), 6.47 (d, *J* =

15.3 Hz, 1 H), 6.23 (tdd, J = 15.3, 10.2, 1.2 Hz, 1 H), 5.81 (td, J = 15.3, 6.9 Hz, 1 H), 3.73 (br s, 2 H), 2.20-2.12 (m, 2 H), 1.47-1.36 (m, 4 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 143.6, 135.7, 131.1, 130.8, 128.2, 126.9, 125.2, 119.1, 116.2, 32.6, 31.6, 22.4, 14.0 (one signal is not seen due to overlap); MS *m/z* (relative intensity) 201 (M^+, 100). HRMS *m/z* 201.1514 (calcd. 201.1517 for $C_{14}H_{19}N$).

***N*-Tosyl-2-[(*E*)-1,3-octadienyl]aniline (Table 1, entry 7)**: mp 114-15 °C; IR (KBr) 3260, 1597, 1162 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2 H), 7.40-7.09 (m, 6 H), 6.68 (s, 1 H), 6.43 (dd, J = 10.2, 15.3 Hz, 1 H), 6.22 (d, J = 15.3 Hz, 1 H), 6.00 (dd, J = 15.3, 10.2 Hz, 1 H), 5.77 (td, J = 7.8, 15.3 Hz, 1 H), 2.35 (s, 3 H), 2.21 (m, 2 H), 1.43-1.25 (m, 4 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.9, 143.2, 137.3, 136.5, 133.1, 133.0, 132.9, 129.9, 128.6, 128.0, 127.2, 126.8, 126.5, 123.6, 32.5, 31.4, 22.4, 21.6, 14.1; MS *m/z* (relative intensity) 355 (M^+, 4), 284 (100); HRMS *m/z* 355.1603 (calcd. 355.1606 for $C_{21}H_{25}NO_2S$).

***N*-Trifluoroacetyl-2-[(*E*)-1-hexenyl]-2,3-dihydroindole (Table 1, entry 8)**: oil; IR (liquid film) 1694, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 7.5 Hz, 1 H), 7.31-7.13 (m, 3 H), 5.59 (td, J = 6.3, 15.3 Hz, 1 H), 5.45 (dd, J = 6.6, 15.3 Hz, 1 H), 5.16-5.11 (m, 1 H), 3.51 (dd, J = 8.7, 15.6 Hz, 1 H), 2.86 (d, J = 15.6 Hz, 1 H), 1.99-1.92 (m, 2 H), 1.32-1.24 (m, 4 H), 0.80 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.5 (q, J = 37 Hz, $\underline{C}OCF_3$), 132.8, 130.9, 128.3, 127.8, 126.0, 125.2, 118.7, 118.1, 114.5 (q, J = 286 Hz, CF_3), 61.9, 36.8, 31.7, 22.1, 13.9, 12.6; MS *m/z* (relative intensity) 297 (M^+, 100); HRMS *m/z* 297.1337 (calcd. 297.1340 for $C_{16}H_{18}F_3NO$).

***N*-Trifluoroacetyl-2-[(*E*)-1,3-octadienyl]aniline (Table 1, entry 8)**: mp 93-4 °C; IR (KBr) 3291, 1704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.92 (br s, 1 H), 7.79 (dd, J = 7.8, 1.8 Hz, 1 H), 7.47 (dd, J = 2.1, 7.2 Hz, 1 H), 7.31-7.20 (m, 2 H), 6.68 (dd, J = 10.2, 15.3 Hz, 1 H), 6.38 (d, J = 15.0 Hz, 1 H), 6.24 (dd, J = 10.5, 15.3 Hz, 1 H), 5.91 (td, J = 7.2, 15.0 Hz, 1 H), 2.21-2.14 (m, 2 H), 1.49-1.33 (m, 4 H), 0.98 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 156.6 (q, J = 37 Hz, $\underline{C}OCF_3$), 138.7, 134.7, 131.3, 131.0, 129.9, 128.1, 127.2, 127.0, 123.7, 122.6, 115.9 (q, J = 286 Hz, CF_3), 32.6, 31.3, 22.4, 14.0; MS *m/z* (relative intensity) 297 (M^+, 40), 128 (100); HRMS *m/z* 297.1334 (calcd. 297.1340 for $C_{16}H_{18}F_3NO$).

***N*-Tosyl-2-[(*E*)-2-buten-2-yl]-2,3-dihydroindole (Table 1, entry 9)**: oil; IR (liquid film) 1597, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, J = 8.5 Hz, 1 H), 7.65 (d, J = 9.6 Hz, 1 H), 7.61 (d, J = 8.1 Hz, 2 H), 7.30-7.10 (m, 4 H), 5.58 (q, J = 6.9 Hz, 1 H), 4.64 (dd, J = 3.9, 10.2 Hz, 1 H), 2.97 (dd, J = 10.2, 16.5 Hz, 1 H), 2.22 (dd, J = 3.9, 16.5 Hz, 1 H). 2.36 (s, 3 H), 1.60 (d, J = 6.9 Hz, 3 H), 1.46 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.8, 142.6, 138.0, 134.5, 132.1, 128.6, 128.5, 126.4, 122.4, 119.6, 117.7, 99.3, 66.7, 33.4, 21.0, 13.6, 12.0; MS *m/z* (relative intensity) 327 (M^+, 100), 272 (10), 172 (69); HRMS *m/z* 327.1287 (calcd. 327.1293 for $C_{19}H_{21}NO_2S$).

***N*-Tosyl-2-[(*E*)-3-methyl-1,3-pentadienyl]aniline (Table 1, entry 9)**: mp 132-3 °C; IR (KBr) 3254, 1587, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2 H), 7.31-7.26 (m, 2 H), 7.21-7.15 (m, 4 H), 6.45 (s, 1 H), 6.44 (d, J = 15.9 Hz, 1 H), 5.99 (d, J = 15.9 Hz, 1 H), 5.63 (q, J = 6.9 Hz, 1 H), 2.36 (s, 3 H), 1.77 (d, J = 6.9 Hz, 3 H), 1.66 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.4, 144.3, 140.8, 135.3, 135.1, 131.0, 130.3, 129.8, 129.7, 129.3, 128.6, 127.0, 124.4, 113.9, 21.0, 11.0, 9.0; HRMS *m/z* 327.1288 (calcd. 327.1293 for $C_{19}H_{21}NO_2S$).

***N*-Trifluoroacetyl-2-[(*E*)-2-buten-2-yl]-2,3-dihydroindole (Table 1, entry 10)**: mp 54-5 °C; IR (KBr) 1689, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.21 (d, J = 7.8 Hz, 1 H), 7.30-7.12 (m, 3 H), 5.26 (q, J = 6.6 Hz,

1 H), 5.05 (d, J = 9.3 Hz, 1 H), 3.53 (dd, J = 9.3, 15.9 Hz, 1 H), 2.88 (d, J = 15.9 Hz, 1 H), 1.56 (s, 3 H), 1.53 (d, J = 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 154.0 (q, J = 37 Hz, $\underline{C}OCF_3$), 142.5, 134.8, 131.1, 127.9, 126.1, 125.2, 119.7, 118.2, 114.3 (q, J = 286 Hz, CF_3), 65.4, 36.0, 13.2, 12.8; MS *m/z* (relative intensity) 269 (M^+, 100); HRMS *m/z* 269.1023 (calcd. 269.1027 for $C_{14}H_{14}F_3NO$).

***N*-Trifluoroacetyl-2-[*(E)*-3-methyl-1,3-pentadienyl]aniline (Table 1, entry 10)**: mp 185-6 °C; IR (KBr) 3054, 1652, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.95 (br s, 1 H), 7.82 (dd, J = 7.5, 1.8 Hz, 1 H), 7.45 (dd, J = 7.2, 1.8 Hz, 1 H), 7.31-7.21 (m, 2 H), 6.70 (d, J = 15.9 Hz, 1 H), 6.37 (d, J = 15.9 Hz, 1 H), 5.78 (q, J = 6.9 Hz, 1 H), 1.86 (s, 3 H), 1.82 (d, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.2 (q, J = 37 Hz, $\underline{C}OCF_3$), 139.5, 134.4, 131.5, 130.8, 127.9, 127.3, 127.1, 123.4, 118.4, 108.1 (q, J = 286 Hz, CF_3), 14.3, 11.9 (one signal is not seen due to overlap); HRMS *m/z* 269.1024 (calcd. 269.1027 for $C_{14}H_{14}F_3NO$).

***N*-Tosyl-2,3-dihydro-2-(2,2-diphenylethenyl)indole (Table 1, entry 11)**: oil; IR (liquid film) 1597, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1 H), 7.45 (d, J = 8.1 Hz, 2 H), 7.40-7.15 (m, 13 H), 7.04-6.99 (m, 2 H), 6.27 (d, J = 9.6 Hz, 1 H), 4.25-4.09 (m, 1 H), 3.09 (dd, J = 7.8, 15.2 Hz, 1 H), 2.89 (dd, J = 5.8, 15.2 Hz, 1 H), 2.29 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.8, 143.6, 142.6, 139.1, 138.9, 138.6, 136.0, 133.7, 132.1, 128.6, 128.5, 128.4, 127.4, 126.4, 122.4, 117.7, 101.8, 58.1, 34.2, 21.0 (several signals are not seen due to overlap); HRMS *m/z* 451.1603 (calcd. 451.1606 for $C_{29}H_{25}NO_2S$).

***N*-Tosyl-2-[*(E)*-4,4-diphenyl-1,3-butadienyl]aniline (Table 1, entry 11)**: mp 197-8 °C; IR (KBr) 3250, 1597, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2 H), 7.45-7.05 (m, 16 H), 6.75-6.48 (m, 4 H), 2.35 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.4, 144.3, 142.3, 140.8, 134.8, 134.3, 131.9, 131.5, 131.0, 130.3, 129.8, 129.7, 129.4, 129.3, 128.6, 128.5, 127.0, 124.4, 120.4, 21.0 (several signals are not seen due to overlap); HRMS *m/z* 451.1601 (calcd. 451.1606 for $C_{29}H_{25}NO_2S$).

***N*-Trifluoroacetyl-2,3-dihydro-2-(2,2-diphenylethenyl)indole (Table 1, entry 12)**: mp 88-9 °C; IR (KBr) 1689, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.22 (d, J = 7.6 Hz, 1 H), 7.50-7.15 (m, 13 H), 6.14 (d, J = 8.7 Hz, 1 H), 5.47-5.24 (m, 1 H), 3.61 (dd, J = 9.3, 15.9 Hz, 1 H), 3.13 (d, J = 15.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 151.3 (q, J = 37 Hz, $\underline{C}OCF_3$), 147.5, 141.0, 138.6, 129.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.5, 126.9, 126.2, 125.1, 120.5, 119.0, 116.8 (q, J = 286 Hz, CF_3), 59.7, 38.5; MS *m/z* (relative intensity) 393 (M^+, 100); HRMS *m/z* 393.1340 (calcd. 393.1340 for $C_{24}H_{18}F_3NO$).

***N*-Trifluoroacetyl-2-[*(E)*-4,4-diphenyl-1,3-butadienyl]aniline (Table 1, entry 12)**: mp 118-9 °C; IR (KBr) 3210, 1698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.86 (br s, 1 H), 7.80 (d, J = 8.1 Hz, 1 H), 7.50-7.15 (m, 13 H), 6.89 (dd, J = 10.5, 14.4 Hz, 1 H), 6.80 (d, J = 10.5 Hz, 1 H), 6.69 (d, J = 14.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 150.7 (q, J = 37.0 Hz, $\underline{C}OCF_3$), 150.8, 142.3, 134.8, 134.7, 134.6, 134.3, 133.5, 131.5, 130.8, 115.6 (q, J = 286 Hz); HRMS *m/z* 393.1342 (calcd. 393.1340 for $C_{24}H_{18}F_3NO$).

***N*-Trifluoroacetyl-2,3-dihydro-2-[*(E)*-3,3-dimethyl-but-1-enyl]indole (Table 1, entries 13 and 14)**: oil; IR (liquid film) 1689, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, J = 7.5 Hz, 1 H), 7.31-7.17 (m, 3 H), 5.62 (d, J = 15.6 Hz, 1 H), 5.34 (dd, J = 7.2, 15.2 Hz, 1 H), 5.20-5.10 (m, 1 H), 3.53 (dd, J = 8.6 , 15.9 Hz, 1 H), 2.86 (d, J = 15.9 Hz, 1 H), 0.95 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 154.0 (q, J = 37 Hz, $\underline{C}OCF_3$), 145.0, 143.9, 128.4, 127.8, 127.3, 127.1, 126.0, 123.7, 116.8 (q, J = 286 Hz, CF_3), 62.5, 37.0, 31.6, 29.2; MS *m/z* (relative intensity) 297 (M^+, 100); HRMS *m/z* 297.1336 (calcd. 297.1340 for $C_{16}H_{18}F_3NO$).

***N*-Trifluoroacetyl-2-[*(E)*-5,5-dimethyl-1,3-hexadienyl]aniline (Table 1, entries 13 and 14)**: oil; IR (liquid film) 3210, 1698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05 (br s, 1 H), 7.80 (d, J = 7.6 Hz, 1 H), 7.48 (dd,

J = 7.5, 1.8 Hz, 1 H), 7.32-7.18 (m, 3 H), 6.42 (d, J = 15.3 Hz, 1 H), 6.02 (t, J = 11.7 Hz, 1 H), 5.60 (d, J = 12.0 Hz, 1 H), 1.22 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 158.3 (q, J = 37 Hz, $\underline{C}OCF_3$), 149.4, 135.3, 128.1,. 127.4, 127.2, 127.1, 126.4, 124.9, 123.6, 122.8, 118.4 (q, J = 286 Hz, $\underline{C}F_3$), 31.6, 29.5; MS *m/z* (relative intensity) 297 (M^+, 100); HRMS *m/z* 297.1334 (calcd. 297.1340 for $C_{16}H_{18}F_3NO$).

***N*-Trifluoroacetyl-2-[*(E)*-2-cyclohexylethenyl]-2,3-dihydroindole (Table 1, entry 15)**: oil; IR (liquid film) 1691, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 7.5 Hz, 1 H), 7.35-7.10 (m, 3 H), 5.56 (dd, J = 6.3, 15.6 Hz, 1 H), 5.39 (dd, J = 6.3, 15.6 Hz, 1 H), 5.16-5.10 (m, 1 H), 3.53 (dd, J = 8.4, 15.6 Hz, 1 H), 2.85 (d, J = 15.6 Hz, 1 H), 2.00-1.50 (m, 5 H), 1.44-1.10 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 152.3 (q, J = 37 Hz, $\underline{C}OCF_3$), 134.9, 130.9, 129.3, 127.2, 126.0, 125.9, 125.2, 123.8, 116.2 (q, J = 286 Hz, CF_3), 73.3, 44.7, 41.0, 32.5, 32.1, 26.2, 26.1, 26.0; MS *m/z* (relative intensity) 323 (M^+, 100); HRMS *m/z* 323.1493 (calcd. 323.1496 for $C_{18}H_{20}F_3NO$).

***N*-Trifluoroacetyl-2-[*(E)*-4-cyclohexyl-1,3-butadienyl]aniline (Table 1, entry 15)**: mp 123-4 °C; IR (liquid film) 3214, 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90 (br s, 1 H), 7.79 (dd, J = 7.6, 1.8 Hz, 1 H), 7.49 (dd, J = 7.6, 1.9 Hz, 1 H), 7.23-7.16 (m, 2 H), 6.68 (dd, J = 15.6, 10.5 Hz, 1 H), 6.40 (d, J = 15.3 Hz, 1 H), 6.22 (ddd, J = 0.6, 10.5, 15.3 Hz, 1 H), 5.87 (dd, J = 6.9, 15.3 Hz, 1 H), 2.13-2.03 (m, 1 H), 1.80-1.60 (m, 4 H), 1.40-1.10 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 156.0 (q, J = 37 Hz, $\underline{C}OCF_3$), 144.3, 135.1, 131.3, 131.0, 128.0, 127.5, 123.7, 122.3, 116.1 (q, J = 286 Hz, CF_3), 41.0, 32.7, 26.0, 25.7 (several signals are not seen due to overlap); MS *m/z* (relative intensity) 323 (M^+, 100); HRMS *m/z* 323.1495 (calcd. 323.1496 for $C_{18}H_{20}F_3NO$).

***N*-Tosyl-2-(17β-acetoxyandrosta-3,5-dien-3-yl)-2,3-dihydroindole (Table 1, entry 17)**: mp 180-2 °C; IR (KBr) 1737, 1597, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70-6.90 (m, 8 H), 5.95 (s, 1 H), 5.51-5.39 (m, 1 H), 4.85-4.52 (m, 2 H), 2.97 (dd, J = 6.3, 20.4 Hz, 1 H), 2.69 (dd, J = 10.2, 20.4 Hz, 1 H), 2.35 (s, 3 H), 2.05 (s, 3 H), 0.90 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.2, 143.5, 142.2, 140.9, 135.6, 135.3, 129.4, 127.6, 127.1, 125.9, 125.1, 124.7, 123.8, 116.2, 115.4, 82.7, 66.8, 51.2, 48.1, 42.4, 36.7, 35.0, 34.6, 34.3, 33.8, 33.0, 31.5, 27.4, 23.4, 21.6, 21.0, 20.5, 18.8, 12.7 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 585 (M^+, 3), 430 (100). Anal. calcd. for $C_{36}H_{43}NO_4S$: H, 7.40; C, 73.81; found: H, 7.53; C, 73.92.

***N*-Tosyl-2,3-dihydro-(4-phenylcyclohex-1-enyl)indole (Table 1, entries 18 and 19)**: oil; IR (liquid film) 1598, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81-7.70 (m, 3 H), 7.40-6.88 (m, 8 H), 7.01 (d, J = 8.1 Hz, 2 H), 5.84 (m, 1 H), 4.71 (dd, J = 6.1, 3.7 Hz, 1 H), 3.05 (dd, J = 16.5, 6.1 Hz, 1 H), 2.84 - 2.56 (m, 2 H), 2.36 (s, 3 H), 2.45 - 1.38 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 146.8, 143.8, 142.2, 137.0, 136.9, 135.9, 131.7, 129.5, 128.4, 127.7, 127.2, 126.1, 124.8, 124.0, 123.2, 116.3, 67.1, 40.1, 34.4, 33.3, 29.5, 24.2, 21.6 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 429 (M^+, 20), 274 (100). Anal. calcd. for $C_{27}H_{27}NO_2S$: H, 6.34; C, 75.49; found: H, 6.41; C, 75.55.

***N*-Tosyl-2-[*(E)*-2-(4-phenylcyclohex-1-enyl)ethenyl]aniline (Table 1, entries 18 and 19)**: mp 146-8 °C; IR (KBr) 3279, 1598 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75-7.10 (m, 13 H), 6.56 (br s, 1 H), 6.48 (d, J = 16.1 Hz, 1 H), 6.11 (d, J = 16.1 Hz, 1 H), 5.95-5.75 (m, 1 H), 2.35 (s, 3 H), 3.15-1.65 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 146.5, 143.8, 136.7, 135.7, 133.6, 131.4, 129.6, 128.7, 128.5, 128.4, 127.9, 127.2, 126.9, 126.7, 126.5, 126.3, 126.27, 119.3, 41.4, 34.2, 29.6, 21.6, 14.1; MS *m/z* (relative intensity) 429 (M^+, 4), 274 (100). Anal. calcd. for $C_{27}H_{27}NO_2S$: H, 6.34; C, 75.49; found: H, 6.39; C, 75.60.

***N*-Tosyl-2,3-dihydro-2-(3,3,5,5-tetramethylcyclohex-1-enyl)indole (Table 1, entry 20)**: oil; IR (liquid film) 1598, 1343 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80-7.65 (m, 3 H), 7.40-7.25 (m, 3 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 5.45 (s, 1 H), 4.60 (dd, *J* = 10.1, 2.3 Hz, 1 H), 3.03 (dd, *J* = 18.2, 10.1 Hz, 1 H), 2.67 (dd, *J* = 18.2, 2.3 Hz, 1 H), 2.35 (s, 3 H), 1.69 (d, *J* = 18.2 Hz, 1 H), 1.54 (d, *J* = 18.2 Hz, 1 H), 1.30 (s, 2 H), 1.10 (s, 3 H), 1.05 (s, 3 H), 0.80 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.3, 143.1, 135.9, 133.9, 133.2, 132.1, 130.1, 128.2, 127.8, 125.3, 124.6, 116.6, 68.1, 50.5, 37.7, 34.9, 33.0, 32.1, 31.7, 31.0, 30.8, 30.1, 22.1; MS *m/z* (relative intensity) 409 (M^+, 15), 254 (100). Anal. calcd. for $C_{25}H_{31}NO_2S$: H, 7.63; C, 73.31; found: H, 7.71; C, 73.39.

***N*-Tosyl-2-[(*E*)-2-(3,3,5,5-tetramethylcyclohex-1-enyl)ethenyl]aniline (Table 1, entry 20)**: mp 140-1 °C; IR (KBr) 3296, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16-7.10 (m, 8 H), 6.60 (br s, 1 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 5.95 (d, *J* = 16.0 Hz, 1 H), 5.51 (s, 1 H), 2.36 (s, 3 H), 1.71 (s, 2 H), 1.36 (s, 2 H), 1.03 (s, 6 H), 0.99 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.7, 141.0, 136.7, 136.6, 133.5, 132.9, 131.9, 129.7, 127.8, 127.1, 126.9, 126.6, 126.4, 118.7, 49.7, 37.9, 33.7, 31.4, 30.4, 30.2, 21.6; MS *m/z* (relative intensity) 409 (M^+, 1), 254 (100). Anal. calcd. for $C_{25}H_{31}NO_2S$: H, 7.63; C, 73.31; found: H, 7.68; C, 73.40.

***N*-Tosyl-2-(4-*tert.*-butylcyclohex-1-enyl)-2,3-dihydroindole (Table 1, entry 21)**: oil; IR (liquid film) 1597, 1171 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68-7.61 (m, 3 H), 7.31-7.13 (m, 3 H), 7.01 (d, *J* = 8.1 Hz, 2 H), 5.85 (br s, 1 H), 4.80-4.60 (m, 1 H), 2.97 (dd, *J* = 10.1, 20.3 Hz, 1 H), 2.68 (dd, *J* = 4.1, 20.3 Hz, 1 H), 2.35 (s, 3 H), 2.15-0.81 (m, 7 H), 0.81 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 143.5, 142.1, 136.6, 135.9, 131.7, 129.36, 127.5, 127.0, 124.6, 124.0, 116.0, 115.4, 67.1, 43.8, 34.3, 32.0, 26.4, 25.0, 24.2, 23.6, 21.4 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 409 (M^+, 20), 254 (100). Anal. calcd. for $C_{25}H_{31}NO_2S$: H, 7.63; C, 73.31; found: H, 7.71; C, 73.27.

***N*-Tosyl-2-[(*E*)-2-(4-*tert.*-butylcyclohex-1-enyl)ethenyl]aniline (Table 1, entry 21)**: oil; IR (liquid film) 3263, 1597, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65-7.10 (m, 8 H), 6.55-6.45 (br s, 1 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 6.00 (d, *J* = 16.0 Hz, 1 H), 5.75-5.55 (m, 1 H), 2.36 (s, 3 H), 2.40-0.95 (m, 7 H), 0.90 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 143.8, 136.6, 135.5, 133.5, 132.9, 132.5, 129.6, 127.7, 127.1, 126.8, 126.5, 126.2, 118.5, 44.2, 32.2, 27.8, 27.2, 25.8, 23.7, 21.6 (one signal is not seen due to overlap); MS *m/z* (relative intensity) 409 (M^+, 2), 254 (100). Anal. calcd. for $C_{25}H_{31}NO_2S$: H, 7.63; C, 73.31; found: H, 7.54; C, 73.38.

***N*-Tosyl-2,3-dihydro-2-[3-methoxyestra-1,3,5(10),17-tetraen-17-yl]indole (Table 1, entry 22)**: oil; IR (liquid film) 1597, 1163, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.79-6.55 (m, 11 H), 5.69-5.55 (m, 1 H), 4.95-4.73 (m, 1 H), 3.75 (s, 3 H), 2.95-2.60 (m, 2 H), 2.29 (m, 3 H), 0.95 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.5, 155.0, 154.4, 143.7, 141.8, 137.9, 135.3, 132.8, 131.9, 129.8, 127.6, 127.0, 126.3, 125.1, 124.7, 116.9, 113.8, 111.4, 60.9, 56.5, 50.3, 47.9, 44.0, 38.3, 34.5, 31.5, 27.6, 26.4, 21.5 17.3, 14.1, 13.8 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 539 (M^+, 21), 384 (57), 272 (100). Anal. calcd. for $C_{34}H_{37}NO_3S$: H, 6.92; C, 75.66; found: H, 7.01; C, 75.76.

***N*-Tosyl-2-(2-carbomethoxycyclopent-1-enyl)-2,3-dihydroindole (Table 1, entry 23)**: oil; IR (liquid film) 1712, 1598 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 8.5 Hz, 2 H), 7.31-7.13 (m, 3 H), 6.99 (d, *J* = 8.5 Hz, 2 H), 5.98 (dd, *J* = 16.4, 5.8 Hz, 1 H), 3.78 (s, 3 H), 3.25 (dd, *J* =16.4, 10.0 Hz, 1 H), 2.95-2.50 (m, 3 H), 2.64 (dd, *J* = 10.0, 5.8 Hz, 1 H), 2.50-2.15 (m, 1 H), 2.34 (s, 3 H), 2.07-1.57 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 159.9, 144.0, 141.9, 134.0, 131.0, 129.5, 127.8, 127.4,

127.38, 124.8, 124.1, 115.9, 65.8, 59.7, 51.3, 35.0, 33.7, 21.3, 15.2; MS *m/z* (relative intensity) 398 (MH^+, 9), 366 (100). Anal. calcd. for $C_{22}H_{23}NO_4S$: H, 5.84; C, 66.48; found: H, 5.94; C, 66.54.

***N*-Tosyl-2-[*(E)*-2-(2-carbomethoxycyclopent-1-enyl)ethenyl]aniline (Table 1, entry 23)**: mp 157-8 °C; IR (KBr) 3295, 1704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76 (d, *J* = 16.0 Hz, 1 H), 7.61 (d, *J* = 8.5 Hz, 2 H), 7.40-7.10 (m, 6 H), 7.05 (br s, 1 H), 6.56 (d, *J* = 16.0 Hz, 1 H), 3.78 (s, 3 H), 2.74 (t, *J* = 7.5 Hz, 2 H), 2.74 (t, *J* = 7.5 Hz, 2 H), 2.27 (s, 3 H), 1.83 (quintuplet, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 166.2, 152.2, 143.9, 136.2, 133.4, 133.2, 130.1, 129.6, 129.3, 128.9, 127.2, 127.1, 126.8, 126.5, 126.3, 51.3, 34.2, 33.9, 21.5, 21.3; MS *m/z* (relative intensity) 398 (MH^+, 4), 366 (100). Anal. calcd. for $C_{22}H_{23}NO_4S$: H, 5.84; C, 66.48; found H, 5.88; C, 66.53.

***N*-Tosyl-2,3-dihydro-2-(3,4-dihydronaphth-1-yl)indole (Table 1, entry 24)**: mp 156-8 °C; IR (KBr) 1597, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.45-6.83 (m, 9 H), 6.29 (br t, *J* = 4.3 Hz, 1 H), 5.31 (br d, *J* = 10.0 Hz, 1 H), 3.09 (dd, *J* =15.6, 10.0 Hz, 1 H), 2.80-2.52 (m, 3 H), 2.34 (s, 3 H), 2.45-2.09 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.9, 141.9, 137.2, 135.4, 135.1, 132.6, 131.9, 129.8, 128.4, 128.0, 127.7, 127.0, 126.1, 125.3, 124.7, 122.1, 117.1, 114.1, 62.2, 36.2, 27.9, 22.8, 21.5; MS *m/z* (relative intensity) 401 (M^+, 40), 272 (55), 246 (100). Anal. calcd. for $C_{25}H_{23}NO_2S$: H, 5.78; C, 74.49; found: H, 5.71; C, 74.54.

***N*-Tosyl-2-[*(E)*-2-(3,4-dihydronaphth-1-yl)ethenyl]aniline (Table 1, entry 24)**: oil; IR (liquid film) 3295, 1597 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2 H), 7.50-7.03 (m, 10 H), 6.76 (d, *J* = 15.0 Hz, 1 H), 6.59 (d, *J* = 15.0 Hz, 1 H), 6.52 (br s, 1 H), 6.11 (t, *J* = 5.4 Hz, 1 H), 2.77 (t, *J* = 8.3 Hz, 2 H), 2.37 (dt, *J* = 8.3, 5.3 Hz, 2 H), 2.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.7, 136.5, 135.7, 133.7, 133.0, 132.8, 130.9, 129.5, 128.2, 127.7, 127.6, 127.2, 127.1, 126.7, 126.3, 125.9, 123.7, 123.4, 29.6, 28.0, 23.2, 21.4 (one signal is not seen due to overlap); MS *m/z* (relative intensity) 402 (MH^+, 10), 275 (9), 247 (100). Anal. calcd. for $C_{25}H_{23}NO_2S$: H, 5.78; C, 74.49; found: H, 5.85; C, 74.50.

***N*-Tosyl-1,2,3,4-tetrahydro-2-[*(E)*-β-styryl]quinoline (Table 1, entry 25)**: oil; IR ($CDCl_3$) 2995, 1599, 1166 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.81 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.31-7.15 (m, 8 H), 7.08 (td, *J* = 7.2, 1.2 Hz, 1 H), 6.97 (dd, *J* = 7.8, 0.9 Hz, 1 H), 6.59 (dd, *J* = 15.9, 1.5 Hz, 1 H), 6.11 (dd, *J* = 15.9, 5.7 Hz, 1 H), 5.07 (qd, *J* = 5.7, 1.5 Hz, 1 H), 2.56-2.45 (m, 1 H), 2.37 (s, 3 H), 1.97-2.08 (m, 1 H), 1.94-1.83 (m, 1 H), 1.73-1.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 143.5, 136.6, 136.5, 135.5, 132.2, 131.2, 129.5, 128.6, 128.4, 127.5, 127.1, 126.7, 126.5, 126.4, 125.5, 125.3, 57.2, 28.2, 24.5, 21.6; HRMS *m/z* 389.1460 (calcd. 389.1450 for $C_{24}H_{23}NO_2S$).

***N*-Tosyl-2-[*(E)*-1-hexenyl]-1,2,3,4-tetrahydroquinoline (Table 1, entries 26 and 27)**: oil; IR ($CDCl_3$) 2927, 1599, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.25-7.15 (m, 3 H), 7.06 (td, *J* = 7.5, 1.2 Hz, 1 H), 6.96 (d, *J* = 7.5 Hz, 1 H), 5.66 (dtd, *J* = 15.6, 6.6, 1.2 Hz, 1 H), 5.34 (ddt, *J* = 15.3, 5.4, 1.2 Hz, 1 H), 4.85 (q, *J* = 5.7 Hz, 1 H), 2.55-2.40 (m, 1 H), 2.37 (s, 3 H), 2.10-1.90 (m, 3 H), 1.85-1.70 (m, 1 H), 1.61-1.50 (m, 1 H), 1.30-1.15 (m, 4 H), 0.82 (t, *J* = 6.9 Hz, 3 H) (traces of the vinylic substitution product are seen as impurities); ^{13}C NMR ($CDCl_3$) δ 143.3, 136.9, 135.7, 132.7, 132.1, 129.4, 128.5, 128.4, 127.1, 126.6, 126.3, 125.0, 56.9, 31.9, 31.2, 28.0, 24.3, 22.1, 21.6, 13.9; HRMS *m/z* 369.1773 (calcd. 369.1763 for $C_{22}H_{27}NO_2S$).

***N*-Tosyl-2-[*(E)*-3,3-dimethyl-1-butenyl]-1,2,3,4-tetrahydroquinoline (Table 1, entry 28)**: oil; IR ($CDCl_3$) 2959, 1599, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71 (d, *J* = 7.2 Hz, 1 H), 7.45 (d, *J* = 8.1 Hz, 2 H),

7.20-7.15 (m, 3 H), 7.06 (td, J = 7.2, 0.9 Hz, 1 H), 6.96 (d, J = 7.5 Hz, 1 H), 5.66 (dd, J = 15.9, 1.5 Hz, 1 H), 5.24 (dd, J = 15.6, 5.7 Hz, 1 H), 4.86 (qd, J = 6.0, 1.2 Hz, 1 H), 2.52-2.41 (m, 1 H), 2.37 (s, 3 H), 2.07-1.97 (m, 1 H), 1.86-1.74 (m, 1 H), 1.61-1.50 (m, 1 H), 0.91 (s, 9 H) (traces of the vinylic substitution product are seen as impurities); ^{13}C NMR ($CDCl_3$) δ 143.4, 143.3, 137.0, 135.7, 132.1, 129.4, 128.3, 127.1, 126.5, 126.2, 125.0, 123.4, 57.1, 32.8, 29.5, 28.4, 24.4, 21.6; HRMS *m/z* 369.1771 (calcd. 369.1763 for $C_{22}H_{27}NO_2S$).

***N*-Tosyl-2-(2-hexenyl)-1,2,3,4-tetrahydroquinoline (Table 1, entry 29)**: oil; IR ($CDCl_3$) 2957, 1599, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 1 H), 7.40 (d, J = 8.1 Hz, 2 H), 7.22 (t, J = 7.8 Hz, 1 H), 7.16 (d, J = 8.1 Hz, 2 H), 7.07 (t, J = 7.5 Hz, 1 H), 6.93 (d, J = 7.5 Hz, 1 H), 5.02 (s, 1 H), 4.84 (s, 1 H), 4.74 (t, J = 6.9 Hz, 1 H), 2.37 (s, 3 H), 2.40-1.20 (m, 10 H), 0.90 (t, J = 7.2 Hz, 3 H) (traces of the vinylic substitution product are seen as impurities); ^{13}C NMR ($CDCl_3$) δ 148.6, 143.4, 136.2, 133.5, 129.9, 129.4, 127.9, 127.1, 126.8, 126.6, 125.4, 110.4, 60.2, 32.2, 30.4, 29.9, 28.2, 25.1, 22.6, 21.6. HRMS *m/z* 369.1764 (calcd. 369.1763 for $C_{22}H_{27}NO_2S$).

***N*-Tosyl-2-[*(E)*-1-ethyl-1-butenyl]-1,2,3,4-tetrahydroquinoline (Table 1, entry 30)**: oil; IR ($CDCl_3$) 2964, 1599, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 1 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.23 (td, J = 6.6, 1.2 Hz, 1 H), 7.15 (d, J = 8.1 Hz, 2 H), 7.08 (dd, J = 7.2, 1.2 Hz, 1 H), 6.93 (d, J = 6.9 Hz, 1 H), 5.35 (t, J = 7.2 Hz, 1 H), 4.66 (t, J = 7.8 Hz, 1 H), 2.37 (s, 3 H), 2.35-2.25 (m, 1 H), 2.05-1.87 (m, 1 H), 1.99 (m, 4 H), 1.74-1.50 (m, 2 H), 1.06 (t, J = 7.5 Hz, 3 H), 0.91 (t, J = 7.5 Hz, 3 H) (traces of the vinylic substitution product are seen as impurities); ^{13}C NMR ($CDCl_3$) δ 143.2, 139.6, 136.5, 136.4, 134.7, 129.3, 128.2, 127.6, 127.1, 126.9, 126.7, 125.4, 61.8, 29.6, 25.6, 21.6, 20.9, 14.5, 14.4, 14.2; HRMS *m/z* 369.1761 (calcd. 369.1763 for $C_{22}H_{27}NO_2S$).

***N*-Tosyl-2,3-dihydro-2-methyl-2-[*(E)*-β-styryl]indole (Table 1, entry 31)**: oil; IR ($CDCl_3$) 2960, 1599, 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.71-7.65 (m, 3 H), 7.40-6.80 (m, 10 H), 6.57 (d, J = 16.2 Hz, 1 H), 6.20 (d, J = 16.8 Hz, 1 H), 3.20 (d, J = 15.9 Hz, 1 H), 3.06 (d, J = 16.2 Hz, 1 H), 2.31 (s, 3 H), 1.92 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.3, 142.0, 138.7, 136.3, 132.2, 129.4, 129.1, 128.5, 128.1, 127.8, 127.7, 127.2, 126.7, 125.0, 122.9, 114.3, 71.5, 45.3, 26.2, 21.5; HRMS *m/z* 389.1456 (calcd. 389.1450 for $C_{24}H_{25}NO_2S$).

***N*-Tosyl-1,2,3,4-tetrahydro-2-methyl-2-[*(E)*-β-styryl]quinoline (Table 1, entry 32)**: oil; IR ($CDCl_3$) 2959, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.69 (dd, J = 8.1, 0.9 Hz, 1 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.35-7.10 (m, 9 H), 7.04 (d, J = 7.5 Hz, 1 H), 6.40 (d, J = 16.2 Hz, 1 H), 6.31 (d, J = 16.2 Hz, 1 H), 2.70-2.55 (m, 2 H), 2.37 (s, 3 H), 2.00-1.88 (m, 1 H), 1.82-1.70 (m, 1 H), 1.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.0, 139.4, 137.6, 136.9, 134.7, 133.0, 129.3, 129.2, 128.5, 128.1, 127.6, 127.5, 126.5, 126.0, 125.9, 62.2, 32.8, 29.8, 28.1, 24.2 (one peak is not seen due to overlap); HRMS *m/z* 403.1617 (calcd. 403.1606 for $C_{25}H_{25}NO_2S$).

***N*-Tosyl-1,2,3,4-tetrahydro-2-methyl-2-[*(E)*-3,3-dimethyl-1-butenyl]quinoline (Table 1, entry 33)**: oil; IR ($CDCl_3$) 2958, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.57 (dd, J = 8.1, 1.2 Hz, 1 H), 7.44 (d, J = 8.4 Hz, 2 H), 7.20-7.12 (m, 3 H), 7.10 (td, J = 7.2, 1.2 Hz, 1 H), 6.90 (d, J = 6.0 Hz, 1 H), 5.47 (d, J = 16.2 Hz, 1 H), 5.35 (d, J = 16.2 Hz, 1 H), 2.60-2.45 (m, 2 H), 2.39 (s, 3 H), 1.80-1.60 (m, 2 H), 1.44 (s, 3 H), 0.85 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 143.0, 139.5, 139.2, 138.3, 130.0, 129.5, 129.3, 128.0, 127.5,

125.8, 125.6, 62.3, 32.7, 32.0, 29.3, 28.6, 24.1, 21.6 (one peak is not seen due to overlap); HRMS *m/z* 383.1909 (calcd. 383.1919 for $C_{23}H_{29}NO_2S$).

General Procedure for the Synthesis of *N*-Tosyl-1,2-dihydro-4-methylquinolines (11) and *N*-Tosyl-2,3-dihydro-2-methylindoles (12). To a solution of *N*-tosyl-*o*-alkenylaniline **2e** or **2f** (0.5 mmol, 1 equiv) and vinylic halide (1.0 mmol, 2 equiv) in DMF (3 mL) were added Na_2CO_3 (1.75 mmol, 3.5 equiv), *n*-Bu_4NCl (0.6 mmol, 1.2 equiv) and $Pd(OAc)_2$ (5 mol %, 0.025 mmol). The reaction mixture was stirred under argon at 100 °C for the appropriate time interval. After the usual work up, the residue was purified by flash column chromatography on silica gel, eluting with *n*-hexane/ethyl acetate mixtures. All reactions were carried out on a 0.5 mmol scale in analogy to the above procedure. The reaction time and the isolated yields are given in Table 3.

***N*-Tosyl-2-benzyl-1,2-dihydro-4-methylquinoline (Table 3, entry 1)**: oil; IR (liquid film) 1600, 1166 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.35-7.12 (m, 10 H), 7.00 (d, *J* = 8.1 Hz, 2 H), 5.33 (dq, *J* = 6.9, 1.2 Hz, 1 H), 4.93 (m, 1 H), 2.70 (dd, *J* =13.5, 7.5 Hz, 1 H), 2.62 (dd, *J* = 13.5, 7.5 Hz, 1 H), 2.30 (s, 3 H), 1.62 (d, *J* = 1.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.0, 137.2, 136.1, 133.0, 131.2, 130.7, 129.8, 129.5, 128.8, 128.2, 128.0, 127.4, 126.6, 126.4, 124.8, 123.2, 55.9, 40.1, 21.5, 17.8; HRMS *m/z* 389.1442 (calcd. 389.1445 for $C_{24}H_{23}NO_2S$).

***N*-Tosyl-1,2-dihydro-4-methyl-2-*n*-pentylquinoline (Table 3, entry 2)**: oil; IR (liquid film) 1598, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.29 (td, *J* = 7.2, 1.2 Hz, 1 H), 7.24-7.19 (m, 3 H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.00 (d, *J* = 8.1 Hz, 2 H), 5.36 (dq, *J* = 5.7, 1.2 Hz, 1 H), 4.63 (m, looks like a quartet, *J* = 6.3 Hz, 1 H), 2.31 (s, 3 H), 1.57 (s, 3 H), 1.49-1.08 (m, 8 H), 0.85 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.9, 136.1, 132.9, 130.8, 129.1, 128.7, 128.3, 127.7, 127.3, 126.5, 125.6, 123.0, 54.9, 33.1, 31.4, 25.1, 22.6, 21.4, 17.8, 14.0; HRMS *m/z* 369.1767 (calcd. 369.1763 for $C_{22}H_{27}NO_2S$).

***N*-Tosyl-1,2-dihydro-4-methyl-2-(2,2-dimethylpropyl)quinoline (Table 3, entry 3)**: oil; IR (liquid film) 1597, 1161 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.31 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.23 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2 H), 7.07 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.01 (d, *J* = 8.1 Hz, 2 H), 5.30 (dq, *J* = 6.0, 1.2 Hz, 1 H), 4.90 (m, 1 H), 2.31 (s, 3 H), 1.51 (d, *J* = 1.2 Hz, 3 H), 1.36-1.07 (m, 2 H), 1.01 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.9, 135.9, 132.9, 131.4, 128.8, 128.6, 127.6, 127.4, 126.7, 126.5, 122.9, 52.6, 45.3, 30.6, 29.9, 21.4, 17.7; HRMS *m/z* 369.1771 (calcd. 369.1763 for $C_{22}H_{27}NO_2S$).

***N*-Tosyl-2-cyclohexylmethyl-1,2-dihydro-4-methylquinoline (Table 3, entry 4)**: oil; IR (liquid film) 1597, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.24 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.21 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 7.07 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.01 (d, *J* = 8.1 Hz, 2 H), 5.34 (dq, *J* = 5.7, 1.2 Hz, 1 H), 4.80-4.75 (m, 1 H), 2.03 (s, 3 H), 1.77-1.61 (m, 4 H), 1.54 (s, 3 H), 1.32-1.23 (m, 4 H), 1.00-0.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.0, 136.1, 132.9, 131.1, 129.2, 128.8, 128.6, 127.8, 127.4, 126.7, 125.9, 123.1, 52.6, 40.4, 33.6, 32.6, 26.6, 26.3, 26.2, 21.5, 17.8; MS *m/z* (relative intensity) 395 (M^+, 3), 298 (100); HRMS *m/z* 395.1923 (calcd. 395.1919 for $C_{24}H_{29}NO_2S$).

***N*-Tosyl-1,2-dihydro-2-methoxycarbonylmethyl-4-methylquinoline (Table 3, entry 5)**: oil; IR (liquid film) 1734, 1599, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.24 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.22 (d, *J* = 8.4 Hz, 1 H), 7.11 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.04 (d,

J = 8.1 Hz, 2 H), 5.46 (dq, J = 6.0, 1.2 Hz, 1 H), 5.20 (q, J = 6.9 Hz, 1 H), 3.69 (s, 3 H), 2.51-2.34 (m, 2 H), 2.32 (s, 3 H), 1.58 (d, J = 1.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.5, 143.3, 135.6, 132.6, 130.7, 130.3, 128.8, 128.4, 128.2, 127.4, 126.9, 123.5, 123.2, 51.9, 51.3, 38.9, 21.5, 17.8; HRMS *m/z* 371.1194 (calcd. 371.1191 for $C_{20}H_{21}NO_4S$).

***N*-Tosyl-1,2-dihydro-4-methyl-2-(2-phenylethyl)quinoline (Table 3, entry 6)**: oil; IR (liquid film) 1597, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70 (dd, J = 7.8, 1.2 Hz, 1 H), 7.27-7.05 (m, 10 H), 7.02 (d, J = 8.1 Hz, 2 H), 5.37 (dq, J = 5.7, 1.2 Hz, 1 H), 4.74-4.70 (m, looks like a quartet, J = 6.3 Hz, 4 H), 2.72-2.84 (m, 2 H), 2.33 (s, 3 H), 1.69-1.61 (m, 2 H), 1.58 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.2, 141.8, 136.0, 132.8, 130.9, 129.6, 128.6, 128.5, 128.5, 128.4, 127.9, 127.4, 126.8, 125.9, 125.2, 123.2, 54.7, 34.7, 31.8, 21.5, 17.8; HRMS *m/z* 403.1616 (calcd. 403.1606 for $C_{25}H_{25}NO_2S$).

***N*-Tosyl-2-[*(E)*-1-heptenyl]-2,3-dihydro-2-methylindole (Table 3, entries 8 and 9)**: oil; IR (liquid film) 1600, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 1 H), 7.20 (d, J = 8.1 Hz, 2 H), 7.15 (t, J = 8.1 Hz, 1 H), 7.07 (d, J = 6.9 Hz, 1 H), 6.94 (t, J = 7.5 Hz, 1 H), 5.70 (dt, J = 15.6, 6.3 Hz, 1 H), 5.58 (d, J = 15.6 Hz, 1 H), 3.10 (d, J = 15.9 Hz, 1 H), 2.95 (d, J = 15.9 Hz, 1 H), 2.37 (s, 3 H), 2.10-1.90 (m, 2 H), 1.77 (s, 3 H), 1.40-1.20 (m, 6 H), 0.88 (t, J = 6.3 Hz, 3 H), ^{13}C NMR ($CDCl_3$) δ 143.2, 142.0, 139.0, 132.8, 130.4, 129.3, 128.4, 127.7, 127.1, 124.9, 122.6, 114.1, 71.7, 45.2, 32.3, 31.5, 28.8, 26.3, 22.6, 21.6, 14.2; HRMS *m/z* 383.1925 (calcd. 383.1919 for $C_{23}H_{29}NO_2S$). In the reaction of *N*-tosyl-*o*-isopropenylaniline with *(E)*-1-bromo-1-hexene (see Table 3, entry 9), the product was isolated along with a small amount of *N*-tosyl-2-[*(E)*-1-hexenyl]-1,2,3,4-tetrahydro-3-methylquinoline (as a 66:34 *cis/trans* mixture), revealed by the following unobscured ^{1}H NMR signals: δ 4.22 (t, J = 5.7 Hz, 0.34 H), 4.80 (dd, J = 7.5, 4.2 Hz, 0.66 H), 5.18 (ddt, J = 15.0, 7.5, 0.9 Hz, 0.66 H), 5.36 (ddt, J = 15.3, 6.9, 1.5 Hz, 0.34 H).

***N*-Tosyl-2,3-dihydro-2-methyl-2-[*(E)*-3-phenyl-1-propenyl]indole (Table 3, entry 10)**: oil; IR (liquid film) 1600, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 1 H), 7.15-7.35 (m, 8 H), 7.07 (d, J = 6.9 Hz, 1 H), 6.94 (t, J = 7.5 Hz, 1 H), 5.87 (dt, J = 15.6, 6.3 Hz, 1 H), 5.76 (d, J = 15.6 Hz, 1 H), 3.27-3.44 (m, 2 H), 3.14 (d, J = 15.9 Hz, 1 H), 2.95 (d, J = 15.9 Hz, 1 H), 2.37 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.3, 141.8, 139.9, 138.9, 134.8, 129.4, 128.6, 128.5, 128.3, 127.7, 127.0, 126.1, 124.9, 122.7, 114.1, 71.7, 45.1, 38.6, 26.1, 21.5 (one signal is not seen due to overlap); HRMS *m/z* 403.1610 (calcd. 403.1606 for $C_{25}H_{25}NO_2S$). The presence of *N*-tosyl-1,2,3,4-tetrahydro-3-methyl-2-[*(E)*-β-styryl]quinoline, as a mixture of stereoisomers (*cis/trans* = 67/33), was revealed in the ^{1}H NMR spectrum by the following unobscured signals: δ 0.98 (d, J = 6.9 Hz, 2.01 H), 1.06 (d, J = 6.6 Hz, 0.99 H), 4.43 (t, J = 7.8 Hz, 0.33 H), 5.04 (dd, J = 7.2, 3.9 Hz, 0.67 H), 5.95 (dd, J = 15.9, 7.5 Hz, 0.67 H), 6.00 (dd, J = 15.9, 6.9 Hz, 0.33 H), 6.61 (dd, J = 15.6, 1.2 Hz, 0.67 H).

***N*-Tosyl-2,3-dihydro-2-methyl-2-[*(E)*-4,4-dimethyl-1-pentenyl]indole (Table 3, entry 11)**: oil; IR (liquid film) 1600, 1164 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H), 7.51 (d, J = 6.6 Hz, 1 H), 7.21 (d, J = 8.1 Hz, 2 H), 7.14 (t, J = 7.2 Hz, 1 H), 7.07 (d, J = 7.2 Hz, 1 H), 6.93 (t, J = 7.5 Hz, 1 H), 5.74 (dt, J = 15.3, 6.9 Hz, 1 H), 5.63 (d, J = 15.3 Hz, 1 H), 3.11 (d, J = 15.6 Hz, 1 H), 2.97 (d, J = 15.6 Hz, 1 H), 2.38 (s, 3 H), 2.00-1.75 (m, 2 H), 1.79 (s, 3 H), 0.87 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 143.2, 142.0, 139.0, 135.3, 129.4, 128.3, 127.9, 127.2, 127.0, 124.9, 122.6, 114.1, 72.0, 46.8, 45.4, 31.2, 29.4, 26.1, 21.6. HRMS *m/z* 383.1910 (calcd. 383.1919 for $C_{23}H_{29}NO_2S$). The presence of *N*-tosyl-1,2,3,4-tetrahydro-3-

methyl-2-[(*E*)-3,3-dimethyl-1-butenyl]quinoline, as a mixture of stereoisomers (*cis/trans* = 67/33), was revealed in the ^{1}H NMR spectrum by the following unobscured signals: δ 4.84 (dd, *J* = 7.5, 3.9 Hz, 0.67 H), 4.24 (t, *J* = 7.5 Hz, 0.33 H), 5.07 (dd, *J* = 15.6, 7.8 Hz, 0.67 H), 5.22 (dd, *J* = 15.6, 7.2 Hz, 0.33 H).

***N*-Tosyl-2,3-dihydro-2-methyl-2-[(*E*)-3-methyl-1-butenyl]indole (Table 3; entries 12, 13 and 14)**: oil; IR (liquid film) 1599, 1166 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 8.1 Hz, 1 H), 7.20 (d, *J* = 8.1 Hz, 2 H), 7.14 (t, *J* = 8.1 Hz, 1 H), 7.08 (d, *J* = 7.2 Hz, 1 H), 6.94 (t, *J* = 7.2 Hz, 1 H), 5.66 (dd, *J* = 15.9, 6.0 Hz, 1 H), 5.57 (d, *J* = 15.9 Hz, 1 H), 3.01 (d, *J* = 15.9 Hz, 1 H), 2.95 (d, *J* = 15.9 Hz, 1 H), 2.37 (s, 3 H), 2.30-2.15 (m, 1 H), 1.76 (s, 3 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 0.92 (d, *J* = 6.6 Hz, 3 H), ^{13}C NMR ($CDCl_3$) δ 143.3, 142.0, 139.2, 136.9, 130.2, 129.3, 128.4, 127.7, 127.0, 124.9, 122.6, 114.1, 71.7, 45.3, 30.8, 26.4, 22.1, 22.0, 21.6; HRMS *m/z* 355.1612 (calcd.355.1606 for $C_{21}H_{25}NO_2S$).

***N*-Tosyl-2-[(*E*)-3-cyclohexyl-1-propenyl]-2,3-dihydro-2-methylindole (Table 3, entry 15)**: oil; IR (liquid film) 1600, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2 H), 7.53 (d, *J* = 7.2 Hz, 1 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 7.15 (dt, *J* = 7.2, 0.9 Hz, 1 H), 7.08 (d, *J* = 7.2 Hz, 1 h), 6.93 (dt, *J* = 7.5, 0.9 Hz, 1 H), 5.69 (dt, *J* = 15.6, 6.0 Hz, 1 H), 5.61 (d, *J* = 15.6 Hz, 1 H), 3.11 (d, *J* = 15.9 Hz, 1 H), 2.96 (d, *J* = 15.9 Hz, 1 H), 2.38 (s, 3 H), 1.98-1.90 (m, 1 H), 1.77-1.83 (m, 1 H), 1.70 (s, 3 H), 1.60-1.66 (m, 5 H), 1.32 -1.23 (m, 4 H), 0.95-0.70 (m, 2 H), ^{13}C NMR ($CDCl_3$) δ 143.3, 142.0, 139.1, 134.1, 129.4, 128.9, 128.5, 127.7, 127.1, 124.9, 122.7, 114.2, 71.9, 45.3, 40.4, 37.9, 33.3, 33.2, 26.6, 26.4, 26.3, 21.6; HRMS *m/z* 409.2068 (calcd. 409.2075 for $C_{25}H_{31}NO_2S$).

***N*-Tosyl-2,3-dihydro-2-methyl-2-[(*E*)-4-phenyl-1-butenyl]indole (Table 3, entry 16)**: oil; IR (liquid film) 1600, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62 (d, *J* = 8.1, 2 H), 7.53 (d, *J* = 7.2 Hz, 1 H), 7.40-7.10 (m, 9 H), 6.96 (t, *J* = 7.2 Hz, 1 H), 5.75 (dt, *J* = 15.6, 6.3 Hz, 1 H), 5.60 (d, *J* = 15.6 Hz, 1 H), 3.05 (d, *J* = 15.9 Hz, 1 H), 2.92 (d, *J* = 15.9 Hz, 1 H), 2.73-2.52 (m, 2 H), 2.38 (s, 3 H), 2.40-2.20 (m, 2 H), 1.70 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 139.1, 135.7, 130.5, 129.2, 128.5, 128.4, 128.1, 127.9, 127.8, 127.1, 126.9, 126.7, 125.9, 125.0, 122.8, 113.5, 71.7, 51.5, 45.2, 39.3, 35.5, 34.2; HRMS *m/z* 417.1769 (calcd.417.1762 for $C_{26}H_{27}NO_2S$).

***N*-Tosyl-2-(5-phenyl-2,4-pentadien-2-yl)aniline (10).** Following the method given earlier, reaction of 0.6 mmol of *N*-tosyl-*o*-isopropenylaniline (1.2 equiv), 0.5 mmol of β-bromostyrene (1.0 equiv), 1.75 mmol of Na_2CO_3 (3.5 equiv), 0.6 mmol of *n*-Bu_4NCl (1.2 equiv) and 5 mol % of $Pd(OAc)_2$ in 3 mL of DMF at 100 °C for 1 h gave, after purification by flash chromatography (88:12 *n*-hexane/ethyl acetate), the product **10** in 40% yield as an 88:12 *Z/E* mixture: IR (liquid film) 3250, 1597, 1160 cm^{-1}; ^{1} H NMR ($CDCl_3$) δ 7.70-7.00 (m, 13 H), 6.85 (s, 0.12 H), 6.81 (s, 0.88 H), 6.58 (d, *J* = 15.6 Hz, 0.88 H), 6.45 (d, *J* = 15.5 Hz, 0.12 H), 6.39 (d, *J* = 10.7 Hz, 0.88 H), 6.30 (dd, *J* = 15.5, 11.0 Hz, 0.12 H), 6.07 (dd, *J* = 15.6, 10.7 Hz, 0.88 H), 5.77 (d, *J* = 11.0 Hz, 0.12 H), 1.86 (s, 0.36 H), 1.82 (s, 2.64 H); ^{13}C NMR of the principal stereoisomer ($CDCl_3$) δ 143.7, 136.8, 136.0, 134.8, 133.7, 133.3, 131.5, 130.5, 129.5, 128.7, 128.5, 128.3, 127.7, 127.2, 126.6, 124.5, 124.7, 25.2, 21.4. The stereochemistry of the *E/Z* mixture was assigned by NOE difference studies.

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