Pergamon

Tetrahedron, Vol. 52, No. 8, pp. 2743-2758, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00011-7

Palladium-catalyzed Annulation of Vinylic Cyclopropanes and Cyclobutanes

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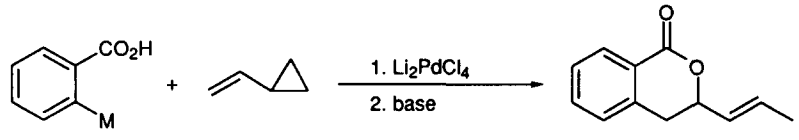
Abstract: Aryl iodides substituted in the *ortho* position by OH, CH_2OH, NH_2, NHTs and $CH(CO_2Et)_2$ groups react with vinylic cyclopropanes and cyclobutanes in the presence of a palladium catalyst and an appropriate base to afford good yields of heterocycles and carbocycles. The annulation products apparently arise by (1) palladium(0) formation and insertion into the carbon-iodine bond of the aryl iodide to generate an arylpalladium intermediate, (2) arylpalladium addition across the carbon-carbon double bond of the alkene, (3) ring-opening of the cyclopropane or cyclobutane by carbon-palladium beta elimination, (4) rearrangement of the resulting unsaturated alkylpalladium compound to a π-allylpalladium compound by a series of reversible palladium hydride beta elimination and readdition steps, (5) anion formation by removal of a proton from the functional group present on the arene, and (6) nucleophilic substitution of the palladium by the resulting anion.

INTRODUCTION

The carbo- and heteroannulation of 1,2-dienes,[1] 1,3-dienes,[2] 1,4-dienes[3] and alkynes[4] by aromatic halides bearing functional groups in the *ortho* position has recently proved to be an extremely versatile method for the synthesis of a wide variety of heterocycles and carbocycles. The diene processes are believed to proceed via π-allylpalladium intermediates. We earlier reported that organopalladium or palladium hydride additions to unsaturated cyclopropanes and cyclobutanes affords a novel route to π-allylpalladium compounds.[5,6] We subsequently employed arylmercury[7] and -thallium[8] compounds bearing functionality in the *ortho* position as precursors to arylpalladium intermediates capable of effecting the heteroannulation of unsaturated cyclopropanes and cyclobutanes (eq 1).



(1)

M = HgX, TlX_2

Unfortunately, the Hg and Tl organometallics suffer several disadvantages when employed in these annulation processes. First of all, they are not as readily available as the corresponding aryl halides. Secondly, such processes required stoichiometric amounts of relatively expensive palladium reagents. Finally, both types of organometallics are toxic and unattractive from an environmental standpoint. It appeared to us that

arylpalladium intermediates produced by the oxidative addition of aryl halides functionalized in the *ortho* position should likewise add to unsaturated cyclopropanes and cyclobutanes to produce π-allylpalladium intermediates that should be readily cyclized to a wide variety of useful heterocycles and carbocycles. Indeed, this has proven to be true as reported in our preliminary communication.[9] We wish at this time to report full details of that study.

RESULTS AND DISCUSSION

We chose to explore carboannulation processes first. A variety of reaction conditions similar to those employed previously by us for the carboannulation of dienes have been examined on the model reaction of diethyl 2-iodophenylmalonate and vinylcyclopropane. Using 5 mol % $Pd(OAc)_2$, 1 equivalent of *n*-Bu_4NCl,[10] 4 equivalents of base, 5 equivalents of alkene, DMF (1 ml per 0.25 mmol of aryl halide) as the solvent, and 5 mol % PPh_3 where appropriate, we have examined the effect of the base, the temperature and the reaction time on the yield of carboannulation product. Our results are summarized in Table 1, entries 1-8. No product was observed when the reactions were run at 60 °C or DMSO was used as the solvent. When the reactions were run in DMF at 80 °C, most reactions appeared to be complete in approximately 3 days. Of the four bases examined in this reaction, NaOAc and KOAc in the absence of PPh_3 gave the best results (entries 1 and 3) and yields of 80-82 % could be obtained. However, in subsequent reactions these reaction conditions did not always turn out to be optimal. The optimal combination of base and phosphine varied with the nature of the aryl halide and the alkene and only some of the better results are included in the table.

We next examined the effect of varying the structure of the alkene on the yield of carbocycle (entries 9-13). Five equivalents of alkene were employed, because of the high volatility of many of these alkenes and the long reaction times and high temperatures required. With the more hindered alkene isopropenylcyclopropane, longer reaction times were required and lower yields were initially observed. Some decarboalkoxylation of the starting diester was also observed in most of these reactions. With this alkene, the results using Na_2CO_3 plus PPh_3 were actually a little better than when the acetate bases were employed in the absence of PPh_3. The yield could be still further increased to 80 % by dropping the reaction temperature to 60 °C and running the reaction for 7 days (entry 9). When the annulation of 1-methyl-1-vinylcyclopropane was examined, lower yields were obtained and no improvements were observed by changing the base or lowering the reaction temperature (entries 10-12). Again, decarboalkoxylation was observed. Since we had previously observed the palladium-promoted ring-opening of cyclobutanes, as well as cyclopropanes, we have briefly examined the annulation of isopropenylcyclobutane. With this substrate, the acetate bases failed completely and only modest yields of carboannulation product could be obtained using Na_2CO_3 plus PPh_3 (entry 13). Raising the temperature above 80 °C resulted in decarboalkoxylation of the starting diester.

We next turned our attention to the heteroannulation of these same unsaturated cyclopropanes and cyclobutanes. The reaction of *o*-iodophenol and isopropenylcyclopropane was chosen for more detailed study (entries 14-21). Four bases, with and without PPh_3, were examined. Yields of about 70 % could be obtained using KOAc, with or without PPh_3, or Na_2CO_3 or K_2CO_3 without PPh_3. Further studies with other iodophenols and alkenes described below indicated that best results are generally obtained using KOAc without PPh_3. Several reactions with *o*-iodophenol and isopropenylcyclopropane still exhibited substantial amounts of starting aryl iodide after 3 days at 80 °C (entries 19-21).

Table 1. Palladium-catalyzed Annulation of Unsaturated Cyclopropanes and Cyclobutanes.

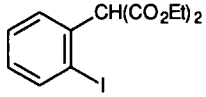
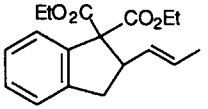
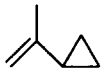
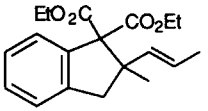
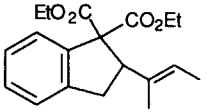
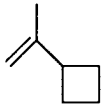
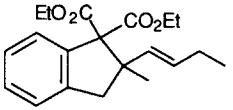
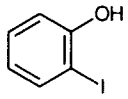
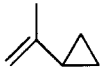
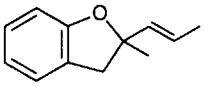
entry	aryl halide	alkene	base	PPh_3	reaction time (d), temp (°C)	product	% yield
1			NaOAc	–	3, 80		82
2			NaOAc	+	3, 80		40
3			KOAc	–	3, 80		80
4			KOAc	+	3, 80		44
5			Na_2CO_3	–	3, 80		61
6			Na_2CO_3	+	3, 80		52
7			K_2CO_3	–	3, 80		26
8			K_2CO_3	+	3, 80		51
9			Na_2CO_3	+	7, 60		80
10			KOAc	–	4, 80		50
11			Na_2CO_3	+	5, 60		51
12			Na_2CO_3	+	4, 80		49
13			Na_2CO_3	+	4, 80		40
14			NaOAc	–	3, 80		39
15			NaOAc	+	3, 80		46
16			KOAc	–	3, 80		70

Table 1. Continued

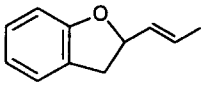
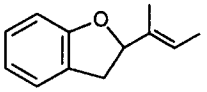
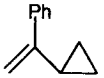
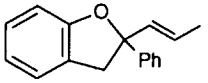
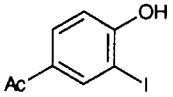
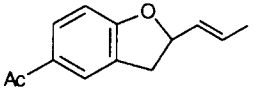
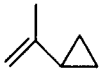
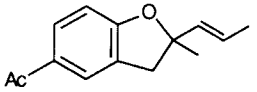
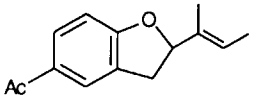
entry	aryl halide	alkene	base	PPh_3	reaction time (d), temp (°C)	product	% yield
17			KOAc	+	3, 80		71
18			Na_2CO_3	–	3, 80		70
19			Na_2CO_3	+	3, 80		39
20			K_2CO_3	–	3, 80		70
21			K_2CO_3	+	3, 80		30
22			KOAc	–	3, 80		70
23			KOAc	+	3, 80		70
24			KOAc	–	3, 100		50
25			KOAc	+	3, 100		53
26			KOAc	–	3, 100		46
27			KOAc	–	3, 80		54
28			KOAc	+	3, 80		56
29			KOAc	–	3, 80		48
30			KOAc	+	3, 80		50
31			KOAc	–	4, 100		41
32			KOAc	+	4, 100		0

Table 1. Continued

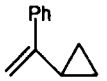
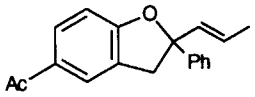
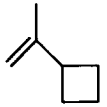
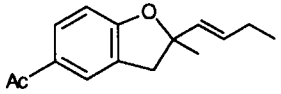
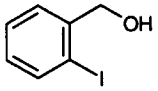
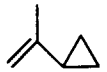
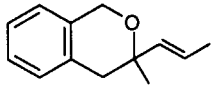
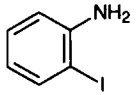
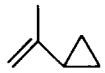
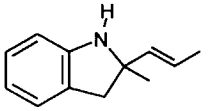
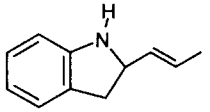
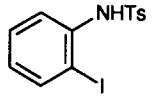
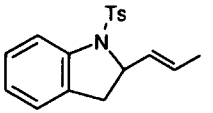
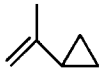
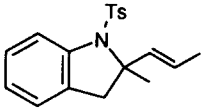
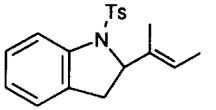
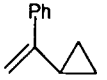
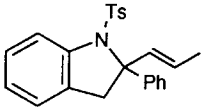
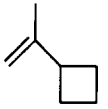
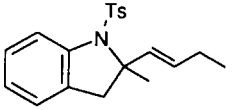
entry	aryl halide	alkene	base	PPh_3	reaction time (d), temp (°C)	product	% yield
33			KOAc	–	3, 100		43
34			KOAc	+	3, 100		36
35			KOAc	–	4, 100		38
36			KOAc	+	4, 100		0
37			KOAc	–	3, 100		53
38			KOAc	+	3, 100		61
39			Na_2CO_3	–	2, 100		0
40			Na_2CO_3	+	2, 100		56
41			K_2CO_3	–	2, 100		0
42			K_2CO_3	+	2, 100		30
43			Et_3N	–	5, 100		68
44			Et_3N	+	5, 100		69
45			Et_3N	+	6, 100		47

Table 1. Continued

entry	aryl halide	alkene	base	PPh_3	reaction time (d), temp (°C)	product	% yield
46			NaOAc	–	4, 100		30
47			KOAc	–	4, 100		77
48			KOAc	+	6, 100		43
49			Na_2CO_3	–	5, 100		18
50			Na_2CO_3	+	5, 100		25
51			K_2CO_3	+	5, 100		45
52			KOAc	–	4, 100		61
53			KOAc	–	3, 100		38
54			KOAc	–	6, 100		37
55			KOAc	–	4, 100		60

Once again, we examined the generality of this heteroannulation process by looking at several other *o*-iodophenols and unsaturated cyclopropanes or cyclobutanes. Using *o*-iodophenol and vinylcyclopropane, yields comparable to those of isopropenylcyclopropane could be obtained (entries 22 and 23). However, lower yields were observed when 1-methyl-1-vinylcyclopropane or 1-cyclopropyl-1-phenylethene were employed (entries 24-26). The reactions of 1-methyl-1-vinylcyclopropane were observed to produce 10-25 % yields of Heck products in which one of the terminal vinylic hydrogens of the alkene has been replaced by the aryl group of the phenol. Apparently, in this case beta hydride elimination by palladium competes effectively with beta carbon elimination. The methyl group present on the cyclopropane apparently hinders alkene addition or the ring-opening process and a higher temperature is now required for this reaction to reach completion.

Annulation reactions of unsaturated cyclopropanes employing 4-acetyl-2-iodophenol generally gave lower yields than *o*-iodophenol (entries 27-36). This may be due to the lower nucleophilicity of this phenoxide, although the overall rate of reaction is comparable to that of *o*-iodophenol. However, 4-acetyl-2-iodophenol gave a cleaner reaction with isopropenylcyclobutane than *o*-iodophenol, allowing isolation of the annulation product in 38 % yield.

In attempting to extend this annulation chemistry to *o*-iodobenzyl alcohol, none of the desired cyclic ether could be obtained from the reaction of vinylcyclopropane, but a 61 % yield of the expected benzopyran could be isolated when isopropenylcyclopropane was employed (entries 37 and 38).

We next turned our attention to the synthesis of nitrogen-containing heterocycles. The reaction of 2-iodoaniline and isopropenylcyclopropane was examined using carbonate and amine bases, with or without PPh_3 (entries 39-44). None of the desired dihydroindole could be isolated when carbonate bases alone were employed, but the addition of PPh_3 resulted in substantially improved yields. Still better yields could be obtained by using Et_3N as the base either with or without PPh_3, although significantly longer reaction times were required. One might hypothesize that the amines or phosphines are required here to prevent chelation of the intermediate *ortho*-palladated aniline (see the subsequent mechanistic discussion).

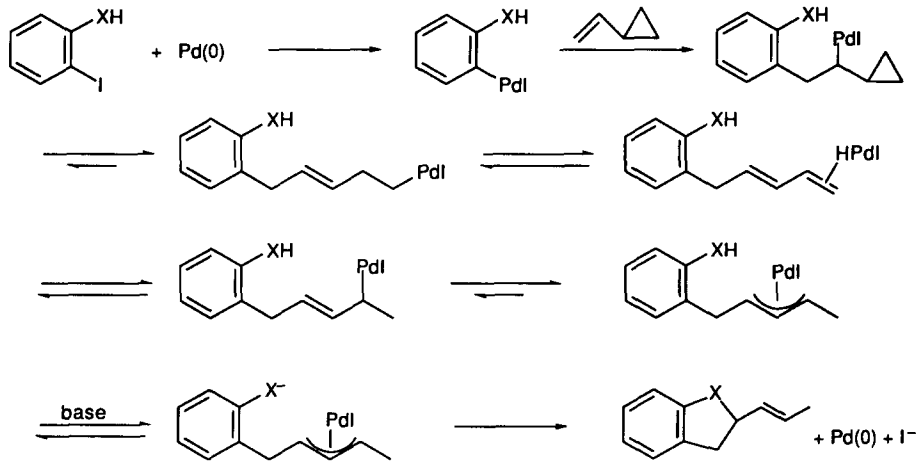
This dihydroindole synthesis was subsequently extended to the annulation of vinylcyclopropane (entry 45). A reasonable 47 % isolated yield was obtained. Unfortunately, efforts to extend this process to 1-cyclopropyl-1-phenylethene and isopropenylcyclobutane failed to afford any of the expected products.

From previous work, it was anticipated that the introduction of a tosyl group on the nitrogen of 2-iodoaniline might substantially improve this process. Thus, *N*-tosyl-2-iodoaniline was prepared and its reactions with unsaturated cyclopropanes and cyclobutanes examined. A variety of acetate and carbonate bases, with or without PPh_3, were studied in the reaction of vinylcyclopropane (entries 46-51). Best results were obtained using KOAc without any PPh_3 (77 % yield, entry 47). This chemistry was subsequently applied to a number of other unsaturated cyclopropanes and cyclobutanes (entries 52-55). In all cases, KOAc in the absence of PPh_3 was observed to give the best results.

This annulation process is believed to proceed as illustrated in Scheme 1. The reduction of $Pd(OAc)_2$ to Pd(0), oxidative addition of the aryl halide to Pd(0), and arylpalladium addition to the alkene are all well known processes.[11] We and others have previously reported the facile ring-opening of cyclopropyl- and cyclobutylcarbinylpalladium species to the corresponding homoallylic and 4-pentenyl palladium species respectively, which rapidly rearrange to the corresponding π-allylpalladium intermediates by a series of palladium hydride beta eliminations and subsequent readditions.[5,6] Generation of the anion corresponding to the

functional group by the base present in the reaction mixture and intramolecular displacement of palladium provide the observed products and regenerate the Pd(0) catalyst.

Scheme 1



CONCLUSION

The palladium-catalyzed hetero- and carboannulation of unsaturated cyclopropanes and cyclobutanes by aryl halides bearing functionality in the *ortho* position provides a novel and efficient process for the synthesis of a wide variety of five- and six-membered ring heterocycles and carbocycles. The process is reasonably general with regard to the types of functional groups on the arene that can be employed and the substitution pattern allowable in the unsaturated cyclopropane or cyclobutane. Different bases, with or without PPh_3, have proven optimal for each different functional group present on the arene. Temperatures of 80-100 °C and reaction times of several days are usually necessary to obtain the best yields. Although the yields are not always real high, the reactions are generally clean and the products easily isolated. Few side-products are observed. While analogous products are obtained by the Pd-catalyzed annulation of 1,3-dienes,[2] this procedure may have advantages when the unsaturated cyclopropanes or cyclobutanes are more readily prepared.

EXPERIMENTAL SECTION

Equipment. The infrared spectra were obtained on an IBM IR/98 FT spectrophotometer, and the ^1H NMR and ^{13}C NMR spectra on a Nicolet NT-300 spectrometer. The GC-MS spectral data were obtained on a Finnegan 4023 GC/MS or a Kratos MS-50 high resolution mass spectrometer. Gas chromatographic analyses were performed using a Varian 3700 gas chromatograph equipped with an OV-101 packed column.

Reagents. All chemicals were used directly as obtained from commercial sources unless otherwise noted. Et_3N and *i*-Pr_2NEt were distilled from KOH pellets. The anhydrous form of $NaHCO_3$, Na_2CO_3, K_2CO_3, NaOAc, and KOAc were all purchased from Fisher-Scientific Co. $Pd(OAc)_2$ was provided by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. 2-Iodophenol, 2-iodoaniline, phenylacetic acid, NaH, 2-iodobenzyl alcohol and PPh_3 were purchased from Aldrich Chemical Co. Inc. *n*-Bu_4NCl was purchased from Lancaster Synthesis.

Preparation of Starting Materials.

Preparation of diethyl 2-iodophenylmalonate. Diethyl 2-iodophenylmalonate was prepared in three steps from phenylacetic acid.[12] Phenylacetic acid (3.50 g, 26 mmol) was iodinated by the thallation/iodination procedure of McKillop et al.[13] to afford 2-iodophenylacetic acid (3.60 g, 58 %) as a white solid: mp 110-112 °C; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 2 H, $ArCH_2$), 6.98 (dt, 1 H, *J* = 7.2, 2.1 Hz, ArH), 7.30 (m, 2 H, ArH), 7.85 (d, 1 H, *J* = 7.8 Hz, ArH).

Ethyl 2-iodophenylacetate was prepared by the method of Harrison[14] from 2-iodophenylacetic acid (1.54 g, 5.9 mmol) to afford the ester as a white solid in 93 % yield: mp 125-126 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3 H, *J* = 7.2 Hz, CH_3), 3.79 (s, 2 H, $ArCH_2$), 4.18 (q, 2 H, *J* = 7.2 Hz, OCH_2), 6.99 (m, 1 H, ArH), 7.35 (m, 2 H, ArH), 7.83 (d, 1 H, *J* = 7.5 Hz, ArH).

Sodium hydride (0.48 g, 20 mmol) was weighed into a flame-dried, 50 ml round-bottom flask equipped with a septum inlet and a magnetic stirring bar. The flask was flushed with N_2. A solution of ethyl 2-iodophenylacetate (2.78 g, 10 mmol) dissolved in diethyl carbonate (20 ml) was added via syringe. The reaction mixture was stirred under N_2 at room temperature overnight. The solution was poured into a cold saturated aqueous solution of NH_4Cl (100 ml) and extracted with CH_2Cl_2. The extracts were dried over $MgSO_4$. Flash column chromatography over silica gel using 5:1 hexanes/ethyl acetate afforded diethyl 2-iodophenylmalonate (3.25 g, 90 %) as a yellow oil: IR (neat) 1753 (C=O), 1736 (C=O), cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 6 H, *J* = 7.2 Hz, CH_3's), 4.25 (m, 4 H, OCH_2's), 5.12 (s, 1 H, ArCH), 7.01 (dt, 1 H, *J* = 7.2, 1.5 Hz, ArH), 7.37 (m, 1 H, ArH), 7.47 (m, 1 H, ArH), 7.87 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 14.1, 29.7, 62.0, 101.6, 128.5, 129.6, 129.7, 136.4, 139.6, 167.7; HRMS calcd for $C_{13}H_{15}IO_4$: 362.0015. Found: 362.0013.

Preparation of vinylcyclopropane. Vinylcyclopropane was prepared via 3-vinyl-1-pyrazoline using the procedure developed by Crawford and Cameron.[15] To a flask containing condensed butadiene (15 ml), a solution containing 3 g of diazomethane dissolved in 15 ml of ethyl ether prepared from 21.5 g of diazald (Aldrich) was added at -78 °C. The reaction was run 2 h at -78 °C. After the reaction mixture stood overnight at ice bath temperatures, the ether was distilled off at atmospheric pressure. The remaining concentrate was distilled at 62 °C/25 mm Hg to provide 4.23 g (44 mmol, 61 %) of 3-vinyl-1-pyrazoline: ^{1}H NMR ($CDCl_3$) δ 1.31-1.38 (m, 1 H, CH), 1.86-1.95 (m, 1 H, CH), 4.23-4.35 (m, 1 H, NCH), 4.59-4.70 (m, 1 H, NCH), 4.89-4.92 (m, 1 H, NCH), 5.30 (dd, 1 H, *J* = 10.4, 1.2 Hz, $=CH_2$), 5.36 (dd, 1 H, *J* = 17.4, 1.2 Hz, =CH-), 5.40 (m, 1 H, =CH-).

3-Vinyl-1-pyrazoline was placed in a flask equipped with a magnetic stirring bar and distillation apparatus and heated in an oil bath kept at 135 °C. Vinylcyclopropane was trapped in a flask kept at -78 °C. Vinylcyclopropane was obtained in 69 % yield: bp 45 °C; ^{1}H NMR ($CDCl_3$) δ 0.36-0.41 (m, 2 H, CH-CH, trans), 0.68-0.74 (m, 2 H, CH-CH, cis), 1.37-1.44 (m, 1 H, -CH-), 4.85 (dd, 1 H, *J* = 10.5, 1.8 Hz, $=CH_2$), 5.07 (dd, 1 H, *J* = 17.3, 1.8 Hz, $=CH_2$), 5.34 (ddd, 1 H, *J* = 17.1, 10.5, 1.8 Hz, =CH-).

Preparation of isopropenylcyclopropane. Isopropenylcyclopropane was prepared by the procedure developed by Corey et al.[16] Sodium hydride (0.1 mol) was placed in a 250 ml three-neck flask and washed several times with hexane. After the system was purged, 25 ml of DMSO was added via syringe, and the mixture was heated at 75-80 °C until the evolution of hydrogen ceased. The resulting solution was cooled in an ice bath, and 17.9 g (0.05 mol) of methyltriphenylphosphonium bromide (Aldrich) dissolved in 50 ml of DMSO was added slowly. The color turned from green to brown upon completion of the addition, and the reaction

mixture was then stirred for 15 min at a temperature of 0-10 °C. Methyl cyclopropyl ketone (4.62 g, 55 mmol, Aldrich) was added slowly and the mixture was warmed to room temperature and stirred for an additional 1 h at that temperature. Distillation of the mixture provided 2.6 g (0.013 mol, 62 %) of isopropenylcyclopropane in a fraction boiling between 70-80 °C: ^{1}H NMR ($CDCl_3$) δ 0.50 (m, 2 H, CH-CH), 0.60 (m, 2 H, CH-CH), 1.42 (m, 1 H, -CH-), 1.65 (s, 3 H, CH_3), 4.70-4.80 (overlapping d, 2 H, J = 1.2 Hz, $=CH_2$).

Preparation of 1-methyl-1-ethenylcyclopropane. 1-Methylcyclopropanecarboxaldehyde was prepared by the oxidation of 1-methylcyclopropanemethanol (Aldrich) using a modification of the procedure reported by Corey et al.[16] To a flask containing 5.06 g (22.5 mmol) of pyridinium chlorochromate in 30 ml of CH_2Cl_2 at room temperature was added 1.28 g (15.0 mmol) of 1-methylcyclopropanemethanol under N_2. The reaction mixture was stirred at room temperature for 2 h and filtered through a florisil column. 1-Methylcyclopropanecarboxaldehyde was distilled at 110 °C to afford a 43 % yield (0.55 g, 6.5 mmol): ^{1}H NMR ($CDCl_3$) δ 0.90 (m, 2 H, CH-CH), 1.14 (m, 2 H, CH-CH), 1.22 (s, 3 H, CH_3), 8.15 (s, 1 H, CHO).

1-Methyl-1-vinylcyclopropane was prepared in a 49 % yield by olefination of 1-methylcyclopropanecarboxaldehyde using the same procedure used for the preparation of isopropenylcyclopropane: ^{1}H NMR ($CDCl_3$) δ 0.9 (m, 2 H, CH-CH), 1.14 (m, 2 H, CH-CH), 1.22 (s, 3 H, CH_3), 4.85 (d, 1 H, J = 10.5 Hz, =CH, trans to the ring), 5.07 (d, 1 H, J = 17.3 Hz, =CH, cis to the ring), 5.34 (dd, 2 H, J = 17.3, 10.5 Hz, =CH-).

Preparation of isopropenylcyclobutane. This compound was prepared in a 49 % yield by olefination of cyclobutyl methyl ketone (Aldrich) using the same procedure used for the preparation of isopropenylcyclopropane: ^{1}H NMR ($CDCl_3$) δ 1.5-2.0 (m, 6 H, CH_2's), 2.50 (s, 3 H, CH_3), 2.80 (m, 1 H, -CH-), 4.50 (s, 1 H, =CH), 4.60 (s, 1 H, =CH).

Preparation of 1-cyclopropyl-1-phenylethene. This compound was prepared in a 50 % yield by olefination of cyclopropyl phenyl ketone (Aldrich) using the same procedure used for the preparation of isopropenylcyclopropane: ^{1}H NMR ($CDCl_3$) δ 0.63 (m, 2 H, CH-CH), 0.85 (m, 2 H, CH-CH), 1.68 (m, 1 H, CH), 4.96 (s, 1 H, $=CH_2$), 5.30 (s, 1 H, $=CH_2$), 7.36 (m, 4 H, ArH), 7.62 (d, 1 H, J = 7.2 Hz, ArH).

Preparation of 4-hydroxy-3-iodoacetophenone. 4-Hydroxy-3-iodoacetophenone was prepared by a procedure reported by Berrios-Peña.[17] To a solution of *p*-hydroxy acetophenone (5.1 g, 38 mmol) (prepared as reported by Schreiber and Stevenson[18]) in concd NH_4OH (250 ml) was added rapidly with stirring a solution of KI (9.63 g) in water (76 ml). After stirring at room temperature overnight, the mixture was filtered. The filtrate was then acidified with concd H_2SO_4 to pH 1 after cooling in an ice bath. The temperature was kept below 35 °C. The heterogeneous solution formed was cooled to 0-5 °C and then filtered. The solid collected was dissolved in ether and treated with activated charcoal. Filtration, concentration, and purification by flash column chromatography (4:1 hexanes/ethyl acetate) gave 5.52 g (56 %) of the desired product. Recrystallization from 1:2 CH_3OH/H_2O afforded 4.86 g (49 %) of 4-hydroxy-3-iodoacetophenone: mp 153-155 °C; IR ($CDCl_3$) 3483 (OH), 1680 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3 H, CH_3CO), 5.91 (s, 1 H, OH), 7.02 (d, 1 H, J = 8.4 Hz, ArH), 7.87 (dd, 1 H, J = 8.4, 2.1 Hz, ArH), 8.30 (d, 1 H, J = 2.1 Hz, ArH).

Preparation of *N*-tosyl-2-iodoaniline.[17] *N*-Tosyl-2-iodoaniline was prepared by a procedure reported by Berrios-Peña.[17] 2-Iodoaniline (5.48 g, 25 mmol) was dissolved in 8 ml of pyridine and solid TsCl (4.77 g, 25 mmol) was added slowly. After the addition of TsCl was completed, the reaction mixture was heated for 1 h at 80 °C in an oil bath. The reaction mixture was then cooled, diluted with Et_2O, and washed with 5 % HCl several times. The organic phase was then dried with $MgSO_4$ and activated charcoal was added. Filtration and

concentration of the filtrate afforded a yellowish solid. Recrystallization of the solid obtained from EtOH afforded 4.9 g (52 %) of the desired product as white crystals: mp 90-92 °C; IR ($CDCl_3$) 3327, 2980, 1339, 1167 cm^{-1}; ^1H NMR (d^6-acetone) δ 2.40 (s, 3 H, CH_3), 6.95 (m, 1 H, ArH), 7.34 (d, 2 H, J = 7.8 Hz, ArH), 7.37 (m, 1 H, ArH), 7.47 (dd, 1 H, J = 8.1, 1.5 Hz, ArH), 7.65 (d, 2 H, J = 8.1, 1.5 Hz, ArH), 7.79 (dd, 1 H, J = 8.1, 1.5 Hz, ArH), 8.0 (br s, 1 H, NH). Anal. calcd for $C_{13}H_{12}INO_2S$: C, 41.82; H, 3.22. Found: C, 41.77; H, 3.47.

General Procedure for the Palladium-catalyzed Annulation of Unsaturated Cyclopropanes and Cyclobutanes.

Palladium acetate (0.0125 mmol), *n*-Bu_4NCl (0.25 mmol), the appropriate base (1.0 mmol), the aryl iodide (0.25 mmol), the alkene (1.25 mmol), DMF (1 ml) and, where indicated, PPh_3 (0.0125 mmol) were added to a 1 dram vial equipped with a stirring bar and teflon-lined screw cap. After heating for the appropriate time, the reaction mixture was diluted with ether (20 ml), washed with satd NH_4Cl (3 x 20 ml) and dried over $MgSO_4$. The reaction mixture was filtered, concentrated and purified by flash column chromatography using hexane-ethyl acetate. The following compounds were obtained using the above general procedure.

1,1-Dicarboethoxy-2-(E-1-propenyl)indane. This compound was obtained as a pale yellow oil in 80 % isolated yield from the reaction of diethyl 2-iodophenylmalonate and vinylcyclopropane using KOAc as a base, and stirring for 3 days at 80 °C (Table 1, entry 3): IR (neat) 2937, 1732, 1477, 1263, 1231, 1051, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (m, 6 H, CH_3's), 1.54 (d, 3 H, J = 6.0 Hz, =C-CH_3), 2.78 (dd, 1 H, J = 15.3, 5.4 Hz, ArCH), 3.17 (dd, 1 H, J = 15.6, 7.6 Hz, ArCH), 3.65 (m, 1 H, -CH-C=), 4.10 (m, 4 H, OCH_2's), 5.35 (m, 1 H, =CH-), 5.45 (m, 1 H, -CH=), 7.15 (m, 3 H, ArH), 7.45 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 14.3, 18.0, 37.5, 49.8, 61.6, 61.2, 69.5, 124.7, 126.7, 126.9, 127.8, 128.5, 129.8, 138.8, 143.7, 169.7; HRMS calcd for $C_{18}H_{22}O_4$: 302.1518. Found: 302.1516.

1,1-Dicarboethoxy-2-methyl-2 (E-1-propenyl)indane. This compound was obtained as a pale yellow oil in 80 % isolated yield from the reaction of diethyl 2-iodophenylmalonate and isopropenylcyclopropane using Na_2CO_3 as a base with PPh_3, and stirring for 7 days at 60 °C (Table 1, entry 9): IR (neat) 3030, 2992, 1750, 1475, 1263, 1227, 1045, 912, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (m, 6 H, CH_3's), 1.30 (s, 3 H, CH_3), 1.64 (dd, 3 H, J = 6.3, 1.5 Hz, =C-CH_3), 2.99 (d, 1 H, J = 15 Hz, ArCH), 3.12 (d, 1 H, J = 15 Hz, ArCH), 4.15 (m, 4 H, OCH_2's), 5.55 (m, 1 H, =CH-), 5.58 (d, 1 H, J = 15.6 Hz, CH=), 7.10-7.30 (m, 3 H, ArH), 7.50 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 14.0, 18.2, 22.4, 44.9, 45.8, 60.9, 61.0, 71.7, 124.0, 124.7, 126.3, 127.5, 128.2, 135.1, 133.4, 144.4, 169.1, 169.3; HRMS calcd for $C_{19}H_{24}O_4$: 316.1675. Found: 316.1677.

1,1-Dicarboethoxy-2-(E-1-methyl-1-propenyl)indane. This compound was obtained as a yellow oil in 51 % isolated yield from the reaction of diethyl 2-iodophenylmalonate and 1-methyl-1-vinylcyclopropane using Na_2CO_3 as a base with PPh_3, and stirring for 5 days at 60 °C (Table 1, entry 11): IR (neat) 2996, 2930, 1726, 1477, 1266, 1234, 1039, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (t, 6 H, J = 7.2 Hz, CH_3's), 1.33 (s, 3 H, CH_3), 1.52 (d, 3 H, J = 7.5 Hz, =C-CH_3), 2.90 (dd, 1 H, J = 7.8, 3.6 Hz, ArCH), 3.33 (dd, 1 H, J = 15.9, 7.8 Hz, ArCH), 3.95 (dd, 1 H, J = 7.8, 3.6 Hz, -CH-), 4.15 (m, 4 H, OCH_2's), 5.45 (q, 1 H, J = 7.5 Hz, =CH-), 7.15-7.25 (m, 3 H, ArH), 7.50 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.2, 14.4, 14.6, 20.1, 36.6, 54.5, 61.1, 61.6, 122.7, 124.1, 126.6, 126.7, 128.5, 135.4, 139.2, 144.3, 169.5, 169.5; HRMS calcd for $C_{19}H_{24}O_4$: 316.1675. Found: 316.1674.

2-(E-1-Butenyl)-1,1-dicarboethoxy-2-methylindane. This compound was obtained as a yellow oil in 40 % isolated yield from the reaction of diethyl 2-iodophenylmalonate and isopropenylcyclobutane using Na_2CO_3 as a base with PPh_3, and stirring for 4 days at 80 °C (Table 1, entry 13): IR (neat) 3028, 2924, 1726, 1477, 1129, 1045, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.19 (m, 6 H, CH_3's), 1.30 (s, 3 H, CH_3), 1.95 (m, 2 H, =C-CH_2), 2.99 (d, 1 H, *J* = 15 Hz, ArCH), 3.19 (d, 1 H, *J* = 15.6 Hz, ArCH), 4.05 (m, 4 H, OCH_2's), 5.56 (d, 1 H, *J* = 15.6 Hz, =CH-), 5.75 (dt, 1 H, *J* = 15.6, 1.2 Hz, CH=C-), 7.22 (m, 3 H, ArH), 7.50 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 14.1, 25.9, 29.8, 31.0, 45.2, 51.9, 60.1, 60.3, 65.9, 71.9, 124.9, 126.4, 127.6, 130.9, 131.2, 133.2, 139.0, 143.5, 169.2, 169.5; HRMS calcd for $C_{20}H_{26}O_4$: 330.1831. Found: 330.1831.

2,3-Dihydro-2-methyl-2-(E-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 71 % isolated yield from the reaction of 2-iodophenol and isopropenylcyclopropane using KOAc as a base with PPh_3, and stirring for 3 days at 80 °C (Table 1, entry 17): IR (neat) 3034, 2928, 2856, 1627, 1597, 1491, 1246, 916, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 3 H, CH_3), 1.70 (d, 3 H, *J* = 5.1 Hz, =C-CH_3), 3.01 (d, 1 H, *J* = 15.3 Hz, ArCH), 3.32 (d, 1 H, *J* = 15.3 Hz, ArCH), 5.65-5.85 (m, 2 H, CH=CH-), 6.75-6.85 (m, 2 H, ArH), 7.10 (t, 2 H, *J* = 7.8 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 26.5, 42.5, 87.5, 109.8, 120.2, 124.2, 125.2, 126.9, 128.1, 134.7, 158.9; HRMS calcd for $C_{12}H_{14}O$: 174.1045. Found: 174.1044.

2,3-Dihydro-2-(E-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 70 % isolated yield from the reaction of 2-iodophenol and vinylcyclopropane using KOAc as a base, and stirring for 3 days at 80 °C (Table 1, entry 22). The IR, ^1H and ^{13}C NMR spectral data for this compound were identical with those previously reported for this compound by Berrios-Peña:[17] IR (neat) 3015, 2928, 2856, 1675, 1615, 1510, 1490, 1260, 1246, 916, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (dd, 3 H, *J* = 6.6, 1.5 Hz, =C-CH_3), 2.97 (dd, 1 H, *J* = 15.6, 8.1 Hz, ArCH), 3.32 (dd, 1 H, *J* = 15.6, 9.3 Hz, ArCH), 5.05 (m, 1 H, O-CH), 5.60-5.75 (m, 1 H, HC=), 5.75-5.95 (dq, 1 H, *J* = 15.3, 6.3 Hz, =CH-), 6.70-6.90 (m, 2 H, ArH), 7.0-7.20 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 36.2, 83.9, 104.5, 120.4, 124.9, 126.7, 128.1, 130.7, 133.5, 159.5; HRMS calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0885.

2,3-Dihydro-2-(E-1-methyl-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 53 % isolated yield from the reaction of 2-iodophenol and 1-methyl-1-vinylcyclopropane using KOAc as a base with PPh_3, and stirring for 3 days at 100 °C (Table 1, entry 25): IR (neat) 2968, 2920, 1697, 1491, 1462, 1232, 916, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (s, 3 H, CH_3), 1.65 (d, 3 H, *J* = 6.6 Hz, =C-CH_3), 3.04 (dd, 1 H, *J* = 15.9, 7.2 Hz, ArCH), 3.24 (dd, 1 H, *J* = 15.9, 9.3 Hz, ArCH), 5.12 (two overlapping doublets, 1 H, *J* = 9.0 Hz, O-CH-), 5.64 (q, 1 H, *J* = 4.2 Hz, =CH-), 6.75-6.90 (m, 2 H, ArH), 7.0-7.20 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.3, 34.3, 88.1, 109.2, 120.2, 122.7, 124.8, 127.1, 128.0, 134.6, 160.0; HRMS calcd for $C_{12}H_{14}O$: 174.1045. Found: 174.1045.

2,3-Dihydro-2-phenyl-2-(E-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 46 % isolated yield from the reaction of 2-iodophenol and 1-cyclopropyl-1-phenylethene using KOAc as a base, and stirring for 3 days at 100 °C (Table 1, entry 26): IR (neat) 3030, 2928, 2856, 1752, 1627, 1470, 1364, 1268, 1107, 912, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (dd, 3 H, *J* = 6.6, 1.5 Hz, =C-CH_3), 3.48 (two doublets, 2 H,

J = 15.6 Hz, $ArCH_2$), 5.67 (m, 2 H, =CH-), 5.90 (d, 1 H, J = 15.6 Hz, CH=), 6.80-6.95 (m, 2 H, ArH), 7.10-7.50 (m, 7 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 43.5, 90.8, 109.6, 120.7, 124.9, 125.6, 126.0, 126.4, 127.3, 128.2, 128.3, 134.7, 144.8, 158.8; HRMS calcd for $C_{17}H_{16}O$: 236.1201. Found: 236.1204.

5-Acetyl-2,3-dihydro-2-(E-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 54 % isolated yield from the reaction of 4-hydroxy-3-iodoacetophenone and vinylcyclopropane using KOAc as a base, and stirring for 3 days at 80 °C (Table 1, entry 27): IR (neat) 2924, 1678, 1605, 1596, 1498, 1368, 1236, 912, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (dd, 3 H, J = 6.6, 0.9 Hz, =C-CH_3), 2.52 (s, 3 H, $COCH_3$), 3.00 (dd, 1 H, J = 15.9, 7.8 Hz, ArCH), 3.35 (dd, 1 H, J = 15.6, 9.0 Hz, ArCH), 5.22 (dd, 1 H, J = 8.1, 7.8 Hz, O-CH), 5.63 (dd, 1 H, J = 21.9, 7.8 Hz, -CH=), 5.84 (m, 1 H, =CH-), 6.65 (d, 1 H, J = 8.1 Hz, ArH), 7.79 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.7, 26.7, 35.3, 85.2, 108.9, 124.0, 125.4, 127.6, 129.8, 130.3, 130.5, 163.6, 196.5; HRMS calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0994.

5-Acetyl-2,3-dihydro-2-methyl-2-(E-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 50 % isolated yield from the reaction of 4-hydroxy-3-iodoacetophenone and isopropenylcyclopropane using KOAc as a base with PPh_3, and stirring for 3 days at 80 °C (Table 1, entry 30): IR (neat) 2928, 2856, 1754, 1674, 1607, 1498, 1375, 1266, 910, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (s, 3 H, CH_3), 1.87 (d, 3 H, J = 5.1 Hz, =C-CH_3), 2.69 (s, 3 H, $COCH_3$), 3.20 (d, 1 H, J = 15.6 Hz, ArCH), 3.35 (d, 1 H, J = 15.6 Hz, ArCH), 5.87 (m, 2 H, CH=CH), 6.94 (d, 1 H, J = 7.8 Hz, ArH), 7.96 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.8, 26.4, 29.8, 41.7, 89.5, 109.0, 109.1, 124.9, 125.8, 127.6, 130.5, 134.2, 163.1, 196.7; HRMS calcd for $C_{14}H_{16}O_2$: 216.1150. Found: 216.1153.

5-Acetyl-2,3-dihydro-2-(E-1-methyl-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 41 % isolated yield from the reaction of 4-hydroxy-3-iodoacetophenone and 1-methyl-1-vinylcyclopropane using KOAc as a base, and stirring for 4 days at 100 °C (Table 1, entry 31): IR (neat) 2924, 1678, 1605, 1498, 1368, 1236, 916, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (s, 3 H, CH_3), 1.65 (d, 3 H, J = 6.6 Hz, =C-CH_3), 2.26 (s, 3 H, $COCH_3$), 3.04 (dd, 1 H, J = 15.9, 7.2 Hz, ArCH), 3.24 (dd, 1 H, J = 15.9, 9.3 Hz, ArCH), 5.12 (two overlapping doublets, 1 H, J = 9.0 Hz, O-CH-), 5.64 (q, 1 H, J = 4.2 Hz, =CH-), 6.75-6.90 (m, 2 H, ArH), 7.03 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.2, 14.0, 26.4, 33.5, 89.4, 108.7, 115.1, 123.4, 125.3, 127.8, 130.5, 133.9, 164.2, 196.7; HRMS calcd for $C_{14}H_{16}O_2$: 216.1150. Found: 216.1148.

5-Acetyl-2,3-dihydro-2-phenyl-2-(E-1-propenyl)benzofuran. This compound was obtained as a yellow oil in 43 % isolated yield from the reaction of 4-hydroxy-3-iodoacetophenone and 1-cyclopropyl-1-phenylethene using KOAc as a base, and stirring for 3 days at 100 °C (Table 1, entry 33): IR (neat) 3030, 2928, 2856, 1754, 1674, 1607, 1498, 1375, 1266, 910, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (dd, 3 H, J = 6.3, 1.5 Hz, =C-CH_3), 2.45 (s, 3 H, $COCH_3$), 3.43 (two doublets, 2 H, J = 15.6 Hz, $ArCH_2$), 5.59 (m, 1 H, =CH-), 5.80 (d, 1 H, J = 16.5 Hz, -CH=), 6.84 (d, 1 H, J = 9.6 Hz, ArH), 7.15-7.41 (m, 6 H, ArH), 7.75 (t, 1 H, J = 9.6 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 17.8, 26.5, 42.6, 92.6, 109.2, 125.5, 125.6, 126.2, 126.5, 127.2, 127.5, 130.6, 131.0, 134.0, 143.9, 162.9, 196.6; HRMS calcd for $C_{19}H_{18}O_2$: 278.1307. Found: 278.1308.

5-Acetyl-2-(E-1-butenyl)-2,3-dihydro-2-methylbenzofuran. This compound was obtained as a yellow oil in 38 % isolated yield from the reaction of 4-hydroxy-3-iodoacetophenone and isopropenylcyclobutane using

KOAc as a base, and stirring for 4 days at 100 °C (Table 1, entry 35): IR (neat) 2932, 1670, 1605, 1498, 1273, 916, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7.5 Hz, CH_3), 1.51 (s, 3 H, CH_3), 2.00 (m, 2 H, =C-CH_2), 2.50 (s, 3 H, $COCH_3$), 3.00 (d, 1 H, J = 15.6 Hz, ArCH), 3.15 (d, 1 H, J = 15.6 Hz, ArCH), 5.60-5.80 (m, 2 H, -CH=CH-), 6.74 (d, 1 H, J = 9.0 Hz, ArH), 7.75 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.4, 25.3, 26.5, 26.7, 41.8, 89.6, 109.2, 125.8, 127.7, 130.5, 130.5, 131.7, 131.9, 163.1, 196.7; HRMS calcd for $C_{15}H_{18}O_2$: 230.1307. Found: 230.1307.

3-Methyl-3-(E-1-propenyl)-1,2-chromene. This compound was obtained as a yellow oil in 61 % isolated yield from the reaction of 2-iodobenzyl alcohol and isopropenylcyclopropane using KOAc as a base with PPh_3, and stirring for 3 days at 100 °C (Table 1, entry 38): IR (neat) 3026, 2923, 2856, 1454, 1376, 1259, 1078, 910, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H, CH_3), 1.64 (d, 3 H, J = 4.8 Hz, =C-CH_3), 2.80 (d, 1 H, J = 16.5 Hz, ArCH), 2.90 (d, 1 H, J = 16.5 Hz, ArCH), 4.75 (s, 2 H, $ArCH_2O$), 5.50 (m, 2 H, CH=CH), 7.00-7.15 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$) δ 18.0, 27.4, 29.8, 37.7, 68.5, 123.9, 125.8, 125.9, 126.3, 128.7, 133.0, 134.3, 134.4; HRMS calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1204.

2,3-Dihydro-2-methyl-2-(E-1-propenyl)indole. This compound was obtained as a yellow oil in 69 % isolated yield from the reaction of 2-iodoaniline and isopropenylcyclopropane using Et_3N as a base with PPh_3, and stirring for 5 days at 100 °C (Table 1, entry 44): IR (neat) 3376, 3028, 2963, 1601, 1485, 1464, 1268, 972, 910, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (s, 3 H, CH_3), 1.70 (d, 3 H, J = 7.2 Hz, =C-CH_3), 2.87 (d, 1 H, J = 15.6 Hz, ArCH), 2.98 (d, 1 H, J = 15.6 Hz, ArCH), 3.71 (br s, 1 H, NH), 5.60-5.75 (m, 2 H, CH=CH), 6.58-6.73 (m, 2 H, ArH), 7.70-7.85 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 26.9, 43.7, 64.1, 109.2, 118.5, 122.3, 124.9, 127.3, 128.1, 137.7, 150.2; HRMS calcd for $C_{12}H_{15}N$: 173.1204. Found: 173.1204.

2,3-Dihydro-2-(E-1-propenyl)indole. This compound was obtained as a yellow oil in 47 % yield from the reaction of 2-iodoaniline and vinylcyclopropane using Et_3N as a base with PPh_3, and stirring for 6 days at 100 °C (Table 1, entry 45): IR (neat) 3376, 3028, 2963, 1601, 1485, 1268, 972, 910, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (d, 3 H, J = 4.8 Hz, =C-CH_3), 2.75 (dd, 1 H, J = 15.3, 7.8 Hz, ArCH), 3.14 (dd, 1 H, J = 15.3, 7.8 Hz, ArCH), 3.25 (br s, 1 H, NH), 4.25 (m, 1 H, NCH), 5.60-5.75 (m, 2 H, CH=CH), 6.58-6.73 (m, 2 H, ArH), 6.90-7.08 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 36.2, 64.3, 107.5, 120.4, 124.9, 126.7, 128.1, 130.7, 133.5, 145.5; HRMS calcd for $C_{11}H_{13}N$: 159.1048. Found: 159.1051.

2,3-Dihydro-2-(E-1-propenyl)-1-tosylindole. This compound was obtained as a yellow oil in 77 % isolated yield from the reaction of *N*-tosyl-2-iodoaniline and vinylcyclopropane using KOAc as a base, and stirring for 4 days at 100 °C (Table 1, entry 47): IR (neat) 3032, 2957, 1598, 1493, 1477, 1354, 1186, 910, 758, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (d, 3 H, J = 6.3 Hz, =C-CH_3), 2.37 (s, 3 H, $ArCH_3$), 2.62 (dd, 1 H, J = 15.9, 9.6 Hz, ArCH), 2.96 (dd, 1 H, J = 15.9, 9.6 Hz, ArCH), 4.75 (m, 1 H, NCH), 5.80-5.85 (m, 2 H, CH=CH), 7.04 (m, 2 H, ArH), 7.22 (m, 3 H, ArH), 7.62 (q, 3 H, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 17.7, 21.6, 35.5, 63.8, 116.8, 124.5, 125.2, 127.2, 127.3, 129.6, 129.7, 130.8, 131.6, 135.7, 141.5, 143.8; HRMS calcd for $C_{18}H_{19}NO_2S$: 313.1136. Found: 313.1132.

2,3-Dihydro-2-methyl-2-(E-1-propenyl)-1-tosylindole. This compound was obtained as a yellow oil in 61 % isolated yield from the reaction of *N*-tosyl-2-iodoaniline and isopropenylcyclopropane using KOAc as a base, and stirring for 4 days at 100 °C (Table 1, entry 52): IR (neat) 3032, 2957, 2871, 1599, 1479, 1360, 1230, 1100, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (dd, 3 H, *J* = 6.3, 1.2 Hz, =C-CH_3), 1.83 (s, 3 H, CH_3), 2.44 (s, 3 H, ArCH_3), 3.01 (d, 1 H, *J* = 15.9 Hz, ArCH), 3.15 (d, 1 H, *J* = 15.9 Hz, ArCH), 5.60-5.80 (m, 2 H, CH=CH), 7.00 (t, 1 H, *J* = 7.2 Hz, ArH), 7.12-7.32 (m, 4 H, ArH), 7.65 (d, 1 H, *J* = 8.4 Hz, ArH), 7.80 (d, 2 H, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 21.6, 26.3, 45.2, 71.6, 114.2, 122.8, 125.0, 125.1, 127.2, 127.7, 128.4, 129.3, 134.3, 139.1, 142.0, 143.3; HRMS calcd for $C_{20}H_{23}NO_2S$: 341.1450. Found: 341.1454.

2,3-Dihydro-2-(E-1-methyl-1-propenyl)-1-tosylindole. This compound was obtained as a yellow oil in 38 % isolated yield from the reaction of *N*-tosyl-2-iodoaniline and 1-methyl-1-vinylcyclopropane using KOAc as a base, and stirring for 3 days at 100 °C (Table 1, entry 53): IR (neat) 3030, 2926, 1600, 1478, 1462, 1354, 1180, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 3 H, CH_3), 1.59 (d, 3 H, *J* = 6.6 Hz, =C-CH_3), 2.35 (s, 3 H, ArCH_3), 2.65 (dd, 1 H, *J* = 16.2, 9.9 Hz, ArCH), 3.00 (dd, 1 H, *J* = 16.2, 9.9 Hz, ArCH), 5.60 (q, 1 H, *J* = 5.7 Hz, =CH-), 7.00 (m, 2 H, ArH), 7.19 (t, 3 H, *J* = 8.1 Hz, ArH), 7.60 (d, 2 H, *J* = 8.4 Hz, ArH), 7.65 (m, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.2, 21.5, 34.3, 68.6, 115.9, 121.5, 124.0, 124.8, 127.1, 127.6, 129.4, 131.5, 134.9, 135.4, 142.3, 143.6; HRMS calcd for $C_{19}H_{21}NO_2S$: 327.1297. Found: 327.1293.

2,3-Dihydro-2-phenyl-2-(E-1-propenyl)-1-tosylindole. This compound was obtained as a yellow oil in 37 % isolated yield from the reaction of *N*-tosyl-2-iodoaniline and 1-cyclopropyl-1-phenylethene using KOAc as a base, and stirring for 6 days at 100 °C (Table 1, entry 54): IR (neat) 3032, 2926, 1599, 1478, 1356, 1168, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86 (dd, 3 H, *J* = 7.8, 1.5 Hz, =C-CH_3), 2.35 (s, 3 H, ArCH_3), 3.34 (d, 1 H, *J* = 16.2 Hz, ArCH), 3.65 (d, 1 H, *J* = 16.2 Hz, ArCH), 5.82 (m, 1 H, =CH-), 6.30 (d, 1 H, *J* = 15.6 Hz, -CH=), 7.00-7.80 (m, 13 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.9, 21.6, 34.3, 68.6, 109.9, 115.9, 121.4, 124.0, 124.8, 126.8, 127.1, 127.3, 127.6, 129.4, 129.5, 131.5, 134.9, 135.4, 142.3, 143.6; HRMS calcd for $C_{24}H_{23}NO_2S$: 389.1450. Found: 389.1450.

2-(E-1-Butenyl)-2,3-dihydro-2-methyl-1-tosylindole. This compound was obtained as a yellow oil in 60 % isolated yield from the reaction of *N*-tosyl-2-iodoaniline and isopropenylcyclobutane using KOAc as a base, and stirring for 4 days at 100 °C (Table 1, entry 55): IR (neat) 3028, 2968, 1601, 1478, 1462, 1360, 1216, 1186, 1032, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.94 (s, 3 H, CH_3), 2.10-2.20 (m, 2 H, =C-CH_2-), 2.54 (s, 3 H, ArCH_3), 3.12 (d, 1 H, *J* = 15.6 Hz, ArCH), 3.27 (d, 1 H, *J* = 15.6 Hz, ArCH), 5.70-5.95 (m, 2 H, CH=CH), 7.10-7.43 (m, 5 H, ArH), 7.74 (m, 1 H, ArH), 7.91 (d, 2 H, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ 13.5, 21.4, 21.6, 25.3, 43.3, 71.7, 114.2, 122.7, 125.0, 127.1, 127.7, 128.4, 129.3, 131.8, 132.0, 139.1, 142.0, 143.4; HRMS calcd for $C_{20}H_{23}NO_2S$: 341.1450. Found: 341.1448.

Acknowledgment

We gratefully acknowledge the National Institutes of Health and the Petroleum Research Fund administered by the American Chemical Society for partial financial support of this research, and Johnson Matthey, Inc. and Kawaken Fine Chemical Co., Ltd. for the $Pd(OAc)_2$.

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(*Received in USA* 18 *September* 1995; *revised* 18 *December* 1995; *accepted* 19 *December* 1995)