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# PALLADIUM-CATALYZED REACTION OF 3-BROMOINDOLE DERIVATIVE WITH ALLYL ESTERS IN THE PRESENCE OF HEXA-*n*-BUTYLDISTANNANE[1]

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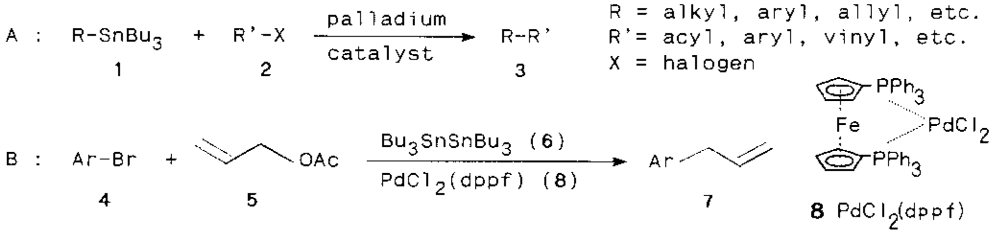
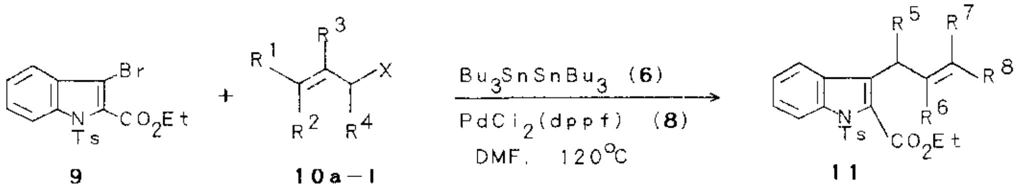
**Abstract**——The palladium-catalyzed cross-coupling reaction of ethyl 3-bromo-1-tosylindole-2-carboxylate (9) with a variety of substituted allylic acetates or carbonates (10) in the presence of hexa-n-butyldistannane (6) gave 3-allylated indoles (11) in high yields.

There are numerous reports[2] concerned with palladium-catalyzed cross-coupling reaction using organostannane (1) as a coupling partner (A in Scheme 1). Although these reactions have advantage of taking place under mild conditions to tolerate a wide variety of reactive functional groups, the starting organostannyl compounds (1) are not always prepared conveniently. Recently, we have reported[3] a new type of cross-coupling reaction, in which aryl bromides (4) directly coupled with allyl acetate (5) in the presence of palladium catalyst (8) and hexa-*n*-butyldistannane (6) (B in Scheme 1). The feature of this reaction is an *in situ* formation of organostannane.[4,5] Since it has a possibility to be a useful synthetic tool to construct a carbon skeleton, we further investigated this reaction to establish the scope and limitation. Here we wish to report the results of this direct allylation of ethyl 3-bromo-1-tosylindole-2-carboxylate (9) with a variety of substituted allyl acetates and carbonates.



Scheme 1

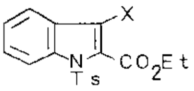


molar ratio; **9** : **10** : **6** : **8** = 1.0 : 1.5 : 1.5 : 0.1

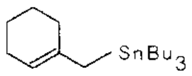
Table Allylation of the Indole (9) with Allyl Acetates or Carbonates (10)

| Run | X | Allyl ester (10)$^{a)}$ $R_1 - R_4$ | Reaction time (min) | Products (11)$^{a)}$ $R^5 - R^8$ | Yield (%)$^{b)}$ |
|---|---|---|---|---|---|
| 1 | OAc | $R^1 = (CH_2)_2Me$ (**10a**) | 270 | $R^8 = (CH_2)_2Me$ (**11a**) | $19^{c)}$ |
| 2 | OAc | $R^4 = Me$ (**10b**) | 90 | $R^8 = Me$ (**11b**) | 59 |
| 3 | OAc | $R^1 = Ph$ (**10c**) | 35 | $R^7$ or $R^8 = Ph$ (**11c**) | $52^{d)}$ |
| 4 | OAc | $R^1 = R^2 = Me$ (**10d**) | 150 | $R^7 = R^8 = Me$ (**11d**) | $7^{e)}$ |
| 5 | OCOOEt | $R^1 = (CH_2)_2Me$ (**10e**) | 100 | $R^8 = (CH_2)_2Me$ (**11a**) | 72 |
| 6 | OCOOEt | $R^2 = (CH_2)_2Me$ (**10f**) | 120 | **11a** | 70 |
| 7 | OCOOEt | $R^4 = (CH_2)_2Me$ (**10g**) | 170 | **11a** | 64 |
| 8 | OCOOEt | $R^3 = Me$ (**10h**) | 80 | $R^6 = Me$ (**11h**) | 93 |
| 9 | OCOOEt | $R^3 = CH_2Ph$ (**10i**) | 150 | $R^6 = CH_2Ph$ (**11i**) | 73 |
| 10 | OCOOEt | $R^1 = R^2 = Me$ (**10j**) | 100 | $R^7 = R^8 = Me$ (**11d**) | $35^{f)}$ |
| 11 | | **10j** | $100^{g)}$ | **11d** | 54 |
| 12 | | **10j** | $90^{h)}$ | **11d** | 45 |
| 13 | OCOOEt | $R^1 - R^3 = -(CH_2)_4-$ (**10k**) | 110 | $R^6 - R^8 = -(CH_2)_4-$ (**11k**) | $33^{i)}$ |
| 14 | | **10k** | $110^{h)}$ | **11k** | 43 |
| 15 | OCOOEt | $R^1 = R^4 = Me$ (**10l**) | $30^{g)}$ | $R^5 = R^8 = Me$ (**11l**) | 60 |

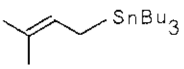
a) Substituents which are not indicated in the Table are hydrogen. b) Isolated yield. c) Accompanied by 9 (35%), 12 (30%), and 13 (9%). d) Accompanied by 16 (38%). e) Accompanied by 12 (24%) and 13 (32%). f) Accompanied by 12 (15%) and 13 (13%). g) 2.0 eq of AcONa were added to the reaction mixture. h) After heating the mixture of 10, 6, and palladium catalyst (8) for 20 min at 120°C, 9 was added to the reaction mixture. Then the whole was heated for the period of time as indicated in the Table. i) Accompanied by 12 (36%).



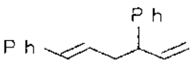
**12** X = H
**13** X = $SnBu_3$



**14**



**15**



**16**

Ethyl 3-bromo-1-tosylindole-2-carboxylate (**9**) was allowed to react with various allylic acetates or carbonates (**10a** – **l**) according to the reported method,[3] and the results are summarized in Table I. The effect of leaving group was obvious, for the reactions with carbonates (**10e** and **10j**) gave better yields than those with acetates (**10a** and **10d**) (Run 1 *vs.* 5 and Run 4 *vs.* 10). Tsuji reported[6] that allylic carbonates were more reactive than acetates on the palladium-catalyzed allylation of C-nucleophile such as $\beta$-keto ester. The reactions proceeded regio- and stereoselectively, since ethyl carbonates of (*E*)- and (*Z*)-2-hexen-1-ol (**10e** and **10f**), and 1-hexen-3-ol (**10g**) which are geometrical or regio isomers with each other, gave the same product (**11a**) in good yields (Runs 5, 6, and 7). Acetate of 1-buten-3-ol (**10b**) also gave the *E*-olefin (**11b**). These results indicated that the substitution occurred at the less substituted end of the allyl moiety with formation of *E* isomer as a result of isomerization or allylic rearrangement of the double bond. The geometry of the products (**11a** and **11b**) was determined on the basis of the coupling constant of vinylic protons ($J$ = 15 Hz). Symmetrical allyl carbonates having an alkyl substituent at $R_3$ (**10h** and **10i**) reacted smoothly to give the products (Runs 8 and 9) in high yields. Conjugate allyl ester, such as cinnamyl acetate (**10c**), also gave the allylated product (**11c**) in 52% yield (Run 3), although the dimeric product (**16**) was formed as a by-product in appreciable amount (38%).[7]

On the contrary to the monosubstituted carbonates (**10e** – **i**), disubstituted carbonates such as prenyl (**10j**) or cyclic allyl carbonate (**10k**) did not give the desired product (**11d** or **k**) in satisfactory yield under the usual condition (Runs 10 and 13). In the case of the reactions giving the allylated products (**11**) in low yields, appreciable amount of the debrominated (**12**) and the stannylated indole (**13**) were formed (Runs 1, 4, 10, and 13).[8] The yield of **11d** was slightly improved by adding sodium acetate in the reaction mixture (Run 11). The yields of **11d** and **11k** were also improved by preparing the allylstannane (**14** and **15**) *in situ*[5] prior to the addition of the 3-bromoindole (**9**) (Runs 12 and 14). $\alpha$-Branched allyl group could also be introduced to the indole (**9**) by the use of 1,3-dimethylallyl carbonate in good yield by the modified procedure (Run 15). It is worth to note that the present results show the possibility for direct introduction of the prenyl or $\alpha$-branched allyl group to aromatic ring from corresponding aryl bromide, since there are many natural products carrying these groups as a side chain on aromatic or heteroaromatic ring.[9]

Further investigation for the application of this direct allylation to various aromatic or heteroaromatic bromides is now in progress.

## ACKNOWLEDGEMENT

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## EXPERIMENTAL

Melting points were determined on a Yanagimoto micro-melting hot-stage apparatus and are uncorrected. Ir spectra were recorded in Nujol mulls (unless otherwise stated) on a Shimadzu IR-400 spectrophotometer. $^1$H-Nmr spectra were recorded on a Hitachi R-24B (60MHz) (unless otherwise stated) and a JOEL GX-400 (400 MHz) spectrometer with tetramethylsilane as an internal reference. Following abbreviations are used: singlet (s), broad singlet (br s), doublet (d), double triplet (dt), triplet (t), quartet (q), and multiplet (m). Mass spectra (ms) were measured with a JEOL JMS-01-SG-2 spectrometer using a direct inlet system. For column chromatography, Merck Kieselgel 60 was used. Allyl acetates (**10a-d**) were commercially available. Allyl carbonates except for **10i** and **10k** were prepared from corresponding commercially available allyl alcohols. A detailed procedure is exemplified as the preparation of **10i**.

### 2-Benzylallyl Ethyl Carbonate (10i)

2-Benzylallyl alcohol: Toluene solution (1.5 M) of diisobutylaluminium hydride (DIBAL) (87 ml, 131 mmol) was slowly added to a solution of ethyl 2-benzylacrylate[10] (10.3 g, 54 mmol) in dry toluene (100 ml) at -78 °C during 30 min, and the resulting solution was stirred for 1 h. The reaction was quenched at -78 °C by careful addition of $H_2O$ (2.5 ml) and saturated $NH_4Cl$ (10 ml), and warmed to room temperature with continuous stirring. Then the mixture was diluted with ether (80 ml) and dried directly by adding powdered $MgSO_4$. The organic layer was collected by suction and the residue was thoroughly washed with ether. The combined organic layers were evaporated to give 2-benzylallyl alcohol as a pale yellow oil (7.99 g), which was used directly in the next reaction. Ir (film): 3330 (OH) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$)$\delta$: 2.34 (1H, br s, OH), 3.38 (2H, s, $C\underline{H}_2Ph$), 3.98 (2H, s, $CH_2O$), 4.87 and 5.10 (each 1H, 2 x s, $C=CH_2$), 7.18 (5H, s, aromatic protons). Ms *m/z*: 148 ($M^+$, 8.3%), 130 (100%).

2-Benzylallyl ethyl carbonate (10i): To an ice-cooled mixture of the above alcohol (5.29 g, 35.7 mmol) and pyridine (8.66 ml, 107 mmol) in dichloromethane (40 ml), was slowly added ethyl chloroformate (8.53 ml, 89.3 mmol). The resulting pale yellow suspension was stirred for 2 h at room temperature. Then the mixture was diluted with dichloromethane (200 ml) and washed successively with 5% HCl, saturated $NaHCO_3$, and saturated NaCl, and dried over $MgSO_4$. After evaporation of the solvent, the resulted pale orange oil (7.90 g) was chromatographed on silica gel with benzene-hexane (1:5) to give the carbonate (10i) as colorless oil (7.12 g, 91% overall), which was distilled under reduced pressure, bp 102 °C (0.4 mmHg). Ir (film): 1745 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$)$\delta$: 1.30 (3H, t, $J$ = 7 Hz, $CH_2C\underline{H}_3$), 3.40 (2H, s, $C\underline{H}_2Ph$), 4.19 (2H, q, $J$ = 7 Hz, $C\underline{H}_2CH_3$), 4.50 (2H, s, $CH_2O$), 4.96 and 5.13 (each 1H, s, $C=CH_2$), 7.18 (5H, s, aromatic protons). Ms *m/z*: 220 ($M^+$,2.4%), 130 (100%). High resolution ms: Calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1098.

### 1-Cyclohexenylmethyl Ethyl Carbonate (10k)

Ethyl 1-cyclohexene-1-carboxylate[11] was reduced with DIBAL, and esterified with ethyl chloroformate as described above to give the title carbonate (10k) as a colorless oil (72% overall), bp 109-112 °C (18 mmHg). Ir (film): 1745 (C=O)$cm^{-1}$. $^1$H-Nmr ($CDCl_3$)$\delta$: 1.28 (3H, t, $J$ = 7 Hz, $CH_2C\underline{H}_3$), 1.2-1.8 and 1.8-2.3 [each 4H, m, $(CH_2)_4$], 4.18 (2H, q, $J$ = 7 Hz, $C\underline{H}_2CH_3$), 4.45 (2H, s, $CH_2O$), 5.72 (1H, br s, CH=C). Ms *m/z*: 94 ($M^+$-90, 66%), 79 (100).

### General Procedure for Allylation of *Ethyl 3-Bromo-1-tosylindole-2-carboxylate (9)*

A mixture of the 3-bromoindole (9, 0.5 mmol), the distannane (6, 0.75 mmol), allyl carbonate (or acetate) (10, 0.75 mmol), and $PdCl_2$(dppf) (8, 0.05 mmol) in dimethylformamide (DMF, 1 ml) was *heated at 120* $^{\circ}$C *for the indicated time in the table.* After cooling to room temperature, the reaction mixture was directly subjected to short chromatography on silica gel with benzene-hexane in order to remove stannyl compound and DMF. The mixture of allylated product (11), debrominated indole (12), stannylated indole (13), and trace amount of unknown stannyl compounds was separated by column chromatography on silica gel with hexane-benzene to give the pure allylated product (11) and by-products (12 and 13). Physical and spectral data of allylated products (11) and by-products (12 and 13) are as follows.

Ethyl 3-[(*E*)-2-hexenyl]-1-tosylindole-2-carboxylate (11a): Colorless oil. *Anal.* Calcd for $C_{24}H_{27}NO_4S$: C, 67.70; H, 6.40; N, 3.29. Found: C, 67.82; H, 6.47; N, 3.35. Ir: 1718 (C=O) $cm^{-1}$. $^1$H-Nmr (400 MHz, $CDCl_3$) $\delta$: 0.81 (3H, t, *J* = 7 Hz, $CH_2CH_2C\underline{H}_3$), 1.29 (2H, q, *J* = 7 Hz, $CH_2C\underline{H}_2CH_3$), 1.41 (3H, t, *J* = 7 Hz, $OCH_2C\underline{H}_3$), 1.90 (2H, q, *J* = 7 Hz, $C\underline{H}_2CH_2CH_3$), 2.29 (3H, s, $SO_2PhC\underline{H}_3$), 3.45 (2H, d, *J* = 6 Hz, indole-$CH_2$), 4.45 ( 2H, q, *J* = 7 Hz, $OC\underline{H}_2CH_3$), 5.3–5.5 (2H, m, $C\underline{H}=C\underline{H}$), 7.15 (2H, d, *J* = 8 Hz, 2 x 3'-H), 7.22 (1H, br t, *J* = 8 Hz, 5 or 6-H), 7.36 (1H, br t, *J* = 8 Hz, 5 or 6-H), 7.47 (1H, d, *J* = 8 Hz, 7-H), 7.75 (2H, d, *J* = 8 Hz, 2 x 2'-H), *8.02 (1H, d, J = 8 Hz, 4-H). Double* irradiation of two methylene protons at 1.90 and 3.45 ppm changed the spectrum of vinylic protons from multiplet to two sets of doublets (*J* = 15 Hz). Ms: *m/z*: 425 ($M^+$, 43.2%), 270 (100%).

Ethyl 3-[(*E*)-2-butenyl]-1-tosylindole-2-carboxylate (11b): *Colorless prisms from ethanol*, mp 55–61 $^{\circ}$C. Ir: 1710 (C=O) $cm^{-1}$. $^1$H-Nmr (400 MHz, $CDCl_3$) $\delta$: 1.42 (3H, t, *J* = 7 Hz, $OCH_2C\underline{H}_3$), 1.59 (3H, br d, *J* = 6 Hz, $CHC\underline{H}_3$), 2.31 (3H, s, $SO_2PhC\underline{H}_3$), 3.44 (2H, br d, *J* = 5.0 Hz, indole-$CH_2$), 4.46 (2H, q, *J* = 7 Hz, $OC\underline{H}_2CH_3$), 5.4–5.6 (2H, m, $C\underline{H}=C\underline{H}$), 7.16 (2H, d, *J* = 8 Hz, 2 x 3'-H), 7.23 (1H, br t, *J* = 6 Hz, 5 or 6-H), 7.36 (1H, br t, *J* = 6 Hz, 5 or 6-H), 7.47 (1H, d, *J* = 7 Hz, 7-H), 7.75 (2H, d, *J* = 8 Hz, 2 x 2'-H), 8.01 (1H, br d, *J* = 7 Hz, 4-H). Double irradiation of methyl and methylene protons at 1.59 and 3.44 ppm changed the spectrum of vinylic protons from multiplet to two sets of doublets (*J* = 15 Hz). Ms *m/z*: 397 ($M^+$, 46.1%), 168 (100%). High resolution Ms: Calcd for $C_{22}H_{23}NO_4S$: 397.1350. Found: 397.1322.

Ethyl 3-($\alpha$-cinnamyl)-1-tosylindole-2-carboxylate (11c): Colorless prisms from methanol, mp 126–128 $^{\circ}$C. *Anal.* Calcd for $C_{27}H_{25}NO_4S$: C, 70.57; H, 5.48; N, 3.05. Found: C, 70.49; H, 5.46; N, 2.99. Ir: 1720 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 1.35 (3H, t, *J* = 7 Hz, $OCH_2C\underline{H}_3$), 2.13 (3H, s, $SO_2PhC\underline{H}_3$), 3.62 (2H, br d, *J* = 5 Hz, indole-$CH_2$), 4.43 ( 2H, q, *J* = 7 Hz, $OC\underline{H}_2CH_3$), 5.9–6.5 (2H, m, $C\underline{H}=C\underline{H}$), 6.9–7.5 (10H, m, aromatic protons) 7.70 (2H, d, *J* = 8 Hz, 2 x 2'-H), 8.00 (1H, br d, *J* = 6 Hz, 4-H). Ms *m/z*: 459 ($M^+$, 0.14%), 258 (100%).

Ethyl 3-prenyl-1-tosylindole-2-carboxylate (11d): Colorless prisms from ethanol, mp 60–61 $^{\circ}$C. *Anal.* Calcd for $C_{23}H_{25}NO_4S$: C, 67.17; H, 6.13; N, 3.41. *Found: C, 67.03; H, 6.12; N, 3.41. Ir: 1710* (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 1.41 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 1.68 and 1.76 [each 3H, 2 x br s, $C=C(CH_3)_2$], 2.30 (3H, s, $SO_2PhC\underline{H}_3$), 3.48 (2H, br d, *J* = 6 Hz, indole-$CH_2$), 4.45 (2H, q, *J* = 7 Hz, $OC\underline{H}_2CH_3$), *5.1–5.3 [1H, m,* $C\underline{H}=C(CH_3)_2$*], 7.0–7.5 (5H, m, aromatic protons)*, 7.75 (2H, d, *J* = 8 Hz, 2 x 2'-H), 8.00 (1H, br d, *J* = 6 Hz, 4-H). Ms *m/z*: 411 ($M^+$, 11.4%), 256 (100%).

Ethyl 3-(2-methylallyl)-1-tosylindole-2-carboxylate (11h): Colorless leaflets from methanol, mp 73–74 $^{\circ}$C. *Anal.* Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5,83; N, 3.52. Found: C, 66.20; H, 5.74; N, 3.51. Ir: 1720 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 1.40 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 1.62 (3H, s, $C=CCH_3$), 2.28 (3H, s, $SO_2PhC\underline{H}_3$), 3.45 (2H, s, indole-$CH_2$), 4.44 (2H, q, *J* = 7 Hz, $C\underline{H}_2CH_3$), 4.68 (2H, br d, $CH_2=C$), 7.0–7.5 (5H, m, aromatic protons), 7.68 (2H, d, *J* = 8 Hz, 2 x 2'-H), 7.98 (1H, br d, *J* = 6 Hz, 4-H). Ms *m/z*: 397 ($M^+$, 46.1%), 169 (100%).

Ethyl 3-(2-benzylallyl)-1-tosylindole-2-carboxylate (**11i**): A colorless oil. *Anal.* Calcd for $C_{28}H_{27}NO_4S$: C, 71.01; H, 5.75; N, 2.96. Found: C, 70.94; H, 5.72; N, 2.98. Ir (film): 1720 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 1.33 (3H, t, $J$ = 7 Hz, $CH_2C\underline{H}_3$), 2.23 (3H, s, $SO_2PhC\underline{H}_3$), 3.24 and 3.43 (each 2H, 2 x s, indole-$C\underline{H}_2CC\underline{H}_2$-phenyl), 4.36 ( 2H, q, $J$ = 7 Hz, $C\underline{H}_2CH_3$), 4.61 and 4.72 (each 1H, 2 x s, $C=CH_2$), 6.9-7.5 (10H, m, aromatic protons), 7.64 (2H, d, $J$ = 7 Hz, 2 x 2'-H), 7.95 (1H, br d, $J$ = 6 Hz, 4-H). Ms *m/z*: 473 ($M^+$, 13.2%), 272 (100%).

Ethyl 3-(1-cyclohexenylmethyl)-1-tosylindole-2-carboxylate (**11k**): Colorless prisms from hexane, mp 94-95 °C. *Anal.* Calcd for $C_{25}H_{27}NO_4S$: C, 68.63; H, 6.22; N, 3.20. Found: C, 68.56; H, 6.20; N, 3.28. Ir: 1730 (C=O) $cm^{-1}$. $^1$H-Nmr (400 MHz, $CDCl_3$) $\delta$: 1.42 (3H, t, $J$ = 7 Hz, $CH_2C\underline{H}_3$), 1.40-1.55 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 1.76 and 1.91 (each 2H, 2 x m, $C=CC\underline{H}_2CH_2$ and $CHC\underline{H}_2CH_2$), 2.31 (3H, s, $SO_2PhC\underline{H}_3$), 3.39 (2H, s, indole-$CH_2$), 4.45 (2H, q, $J$ = 7 Hz, $C\underline{H}_2CH_3$), 5.36-5.38 (1H, m, $C\underline{H}=C$), 7.14 (2H, d, $J$ = 8 Hz, 2 x 3'-H), 7.22 (1H, dt, $J$ = 7 and 1 Hz, 5- or 6-H), 7.36 (1H, dt, $J$ = 7 and 1 Hz, 5- or 6-H), 7.47 (1H, d, $J$ = 8 Hz, 7-H), 7.70 (2H, d, $J$ = 8 Hz, 2 x 2'-H), 8.03 (1H, d, $J$ = 8 Hz, 4-H). Ms *m/z*: 437 ($M^+$, 5.0%), 236 (100%).

Ethyl 3-[(*E*)-1-methyl-2-butenyl]-1-tosylindole-2-carboxylate (**11l**): Colorless prisms from hexane, mp 74-77 °C. *Anal.* Calcd for $C_{23}H_{25}NO_4S$: C, 67.17; H, 6.13; N, 3.41. Found: C, 67.09; H, 6.20; N, 3.41. Ir: 1690 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 1.38 (3H, d, $J$ = 7 Hz, indole-$CHC\underline{H}_3$), 1.43(3H, t, $J$ = 7 Hz, $CH_2C\underline{H}_3$), 1.63( 3H, dt, $J$ = 6 and 2 Hz, $C=CHC\underline{H}_3$), 2.32 (3H, s, $SO_2PhC\underline{H}_3$), 3.77-3.87 (1H, m, indole-CH), 4.46 (2H, q, $J$ = 7 Hz, $OC\underline{H}_2CH_3$), 5.37-5.48 and 5.62-5.72 (each 1H, 2 x m, $C\underline{H}=C\underline{H}$), 7.16 (2H, d, $J$ = 8 Hz, 2 x 3'-H), 7.20 (1H, dt, $J$ = 7 and 1 Hz, $C_5$- or $C_6$-H), 7.34 (1H, dt, $J$ = 7 and 1 Hz, $C_5$- or $C_6$-H), 7.55 (1H, d, $J$ = 8 Hz, $C_7$-H), 7.75 (2H, d, $J$ = 8 Hz, 2 x 2'-H), 8.01 (1H, d, $J$ = 8 Hz, $C_4$-H). Double irradiation of methyl and methine protons at 1.63 and 3.87 ppm changed the spectrum of vinylic protons from multiplet to two sets of doublets ($J$ = 15 Hz). Ms *m/z*: 411 ($M^+$, 11.4%), 256 (100%).

Ethyl 1-tosylindole-2-carboxylate (**12**): Colorless needles, mp 98-99 °C. *Anal.* Calcd for $C_{18}H_{17}NO_4S$: C, 62.96; H, 4.99; N, 4.08. Found: C, 62.98; H, 4.92; N, 3.99. Ir: 1735 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 1.39 (3H, t, $J$ = 7 Hz, $CH_2C\underline{H}_3$), 2.35 (3H, s, $SO_2PhC\underline{H}_3$), 4.40 (2H, q, $J$ = 7 Hz, $C\underline{H}_2CH_3$), 7.1-7.7 (6H, m, aromatic protons), 7.8-8.2 (3H, m, 2 x 2'-H and 4-H). Ms *m/z*: 343 ($M^+$, 13.2%), 143 (100).

Ethyl 1-tosyl-3-(tributylstannyl)indole-2-carboxylate (**13**): Colorless leaflets, mp 68-63 °C. *Anal.* Calcd for $C_{30}H_{43}NO_4SSn$: C, 56.98; H, 6.85; N, 2.21. Found: C, 56.72; H, 6.79; N, 2.12. Ir: 1715 (C=O) $cm^{-1}$. $^1$H-Nmr ($CDCl_3$) $\delta$: 0.6-1.9 (30H, m, $Sn\underline{Bu}_3$, and $OCH_2C\underline{H}_3$), 2.28 (3H, s, $SO_2PhC\underline{H}_3$), 4.40 ( 2H, q, $J$ = 7 Hz, $C\underline{H}_2CH_3$), 7.0-7.6 (5H, m, aromatic protons), 7.71 (2H, d, $J$ = 8 Hz 2 x 2'-H), 8.00 (1H, br d, $J$ = 6 Hz, 4-H). Ms *m/z*: 576 ($M^+$-$C_4H_9$, 100%).

## REFERENCES AND NOTES

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