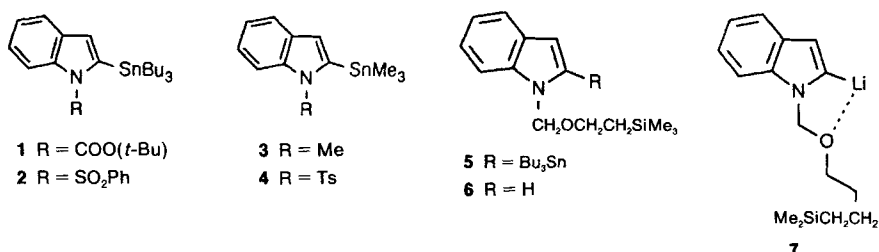


Pd-Catalyzed cross-coupling of a (1*H*-indol-2-yl)stannane **A** with suitable halogenated partners **B** (e.g., sp^2 (aryl and vinyl)-, sp (alkynyl)-, and sp^3 (alkyl)-hybridised halides), the *Stille* reaction, should in principle serve as an alternative (and complementary) route to some of these important intermediates (*Scheme 1*) [5]. Although considerable attention was devoted to the investigation of reactivity of several (heteroaryl)stannanes¹⁾, apparently much less interest was shown for the chemistry of 1*H*-indol-2-yl analogues. To our knowledge, only two reports concerning the preparation of 1*H*-indol-2-yl derivatives (*i.e.* **1–4**) were recently published [7] [8], whereas no report dealing with the use for *Stille* reaction appeared.

In this paper, we will highlight the ability of the protected 2-(tributylstannyl)-1*H*-indole **5** to act as an indol-2-yl-anion equivalent, thereby extending the range of available analogues yet further.

Discussion. – α -Metallation followed by electrophilic trapping has become a powerful method in regioselective functionalization of azoles. This method requires protection of the N-atom and deprotection, and after some experimentation, we opted for the [2-(trimethylsilyl)ethoxy]methyl protecting group ($\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OCH}_2$). This group was successfully introduced at N(1) of indoles prior to metallation [9] and easily removed under very mild conditions such as on treatment with 1*M* Bu_4NF in THF.



Thus, the N(1)-protected tributylstannane **5** was easily prepared on a multigram scale in excellent yield by metallation (1.2 equiv. of BuLi, THF, -10°) of **6** [9a], followed by quenching of the pale-orange lithio complex **7** with 1.3 equiv. of Bu_3SnCl at -20° . The metallation was selectively directed to the C(2) position due to a strong proximity effect of both the N(1)- and O-atom (*i.e.*, the stabilization of **7** related to the electron-withdrawing effect of N(1) as well as to the O-chelation). Stannane **5** was easily purified by filtration through alumina and could be stored at 0° for several weeks without significant decomposition (as judged by ^{119}Sn , ^1H -NMR spectroscopy²⁾).

To illustrate the reagent's versatility, a number of aryl, heteroaryl, vinyl, and allyl-(benzyl) indoles were synthesized using **5** according to *Scheme 1*, emphasis being on difficult cases (see **8–19**, **22** (from **21**), **24** (from **23**), **26** (from **25**), **28** (from **27**), **30** (from **29**), **31–40**, **42** (from **41**), and **43**; *Table*). Optimized isolated yields in a number of test cases ranged from 45 to 95%, after reaction times of 1 to 76 h and simple isolation and side-product removal.

Our initial studies were carried out with iodobenzene (PhI) as halide model, which afforded a 63% yield of **8** upon coupling with **5** using 10 mol-% of $[\text{PdCl}_2(\text{MeCN})_2]$ at room temperature (16 h) in DMF as solvent (*Method A*). The major by-product (25%) in this case was the bi-indole **13** arising from oxidative dimerization of **5** (*Entry 1*). A number of variations in solvent (THF, DMF, CH_2Cl_2 , toluene, and CHCl_3) and molar ratio was also explored. In general, DMF provided the cleanest and faster reaction, while ratios of PhI/**5** as high as 5.0 did not inhibit the oxidative homocoupling. Finally, we found that switching to Pd^0 complexes, *e.g.* $[\text{Pd}(\text{PPh}_3)_4]$ (10%) in DMF (110°) led to

²⁾ The ^{119}Sn , ^1H -NMR spectrum (CDCl_3) of **5** exhibited a single peak at -57.87 ppm.

Table. *Pd-Catalyzed Coupling of Stannane 5 with Halides*

Entry	Method ^{a)}	Halide	Product (yield) [%]	Time [h]
1	A	PhI	8 (63)	16
2	B	PhI	8 (98)	5
3	B	2-NO ₂ -C ₆ H ₄ I	9 (97)	6
4	B	2-Me-C ₆ H ₄ I	10 (93)	2
5	B	4-MeO-C ₆ H ₄ I	11 (56)	3
6	A	4-bromoacetophenone	12 (97)	1
7	B	4-bromoacetophenone	12 (97) ^{b)}	24
8	B	5-bromo-1,2-dihydroacenaphthylene	14 (97)	5
9	B	9-bromoanthracene	15 (95)	6
10	A	2-bromopyridine	16 (19)	72
11	B	2-bromopyridine	16 (80)	72
12	B	2,6-dibromopyridine	17 (92) ^{c)}	24
13	A	2-bromothiophene	18 (62)	16
14	B	2-bromothiophene	18 (88)	6
15	A	3-iodo-1 <i>H</i> -indole	19 (45)	3
16	B	3-iodo-1 <i>H</i> -indole	19 (65)	5
17	B	20	13 (96)	2
18	B	21	22 (94)	3
19	B	23	24 (92)	2
20	A	25	26 (53)	3
21	B	25	26 (89)	3
22	B	27	28 (96)	3
23	B	29	30 (85)	4
24	A	BrCH=CHCO ₂ Me ^{d)}	31 (68) ^{e)}	1
25	B	BrCH=CHCO ₂ Me ^{d)}	31 (87) ^{b)c)}	2
26	B	BrCH=CHSiMe ₃ ^{f)}	32 (93) ^{b)g)}	1
27	B	CH ₂ =C(Br)CO ₂ Et	33 (55) ^{h)}	0.5
28	A	2-bromocyclopent-2-en-1-one	34 (10)	72
29	B	2-bromocyclopent-2-en-1-one	34 (92)	6
30	A	3-bromocyclohex-2-en-1-one	35 (50)	48
31	B	3-bromocyclohex-2-en-1-one	35 (87)	4
32	A	2-bromo-3-ethoxycyclohex-2-en-1-one	36 (N.R.)	72
33	B	2-bromo-3-ethoxycyclohex-2-en-1-one	36 (42)	1
34	B	Me ₃ SiC≡CI	37 (88) ^{b)}	1
35	B	geranyl bromide	39 (12)	72
36	C	geranyl bromide	39 (75)	76
37	C	PhCH ₂ Br	40 (95)	3
38	B	41	42 (20)	24
39	C	41	42 (95)	2
40	C	allyl bromide	43 (93)	6

^{a)} *Method A*: halide/**5** = 1.3, [PdCl₂(MeCN)₂] (10 mol-%), DMF, r.t.; *Method B*: halide/**5** = 1.3, [Pd(tp₄)₄] (10 mol-%), DMF, 110° (unless otherwise stated); *Method C*: halide/**5** = 1.3, [Pd₂(dba)₃] (5 mol-%), tri(fur-2-yl)phosphine (20 mol-%) THF, 60°.

^{b)} Run at 90°.

^{c)} **5**/halide = 2.5.

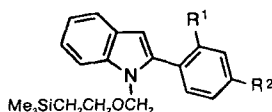
^{d)} (Z)/(E) 7:1.

^{e)} (Z)/(E) 1.5:1.

^{f)} (E)/(Z) 9:1.

^{g)} (E) > 95%.

^{h)} Run in a sealed tube.



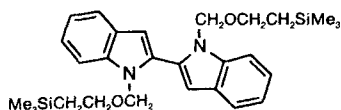
8 $R^1 = R^2 = H$

9 $R^1 = NO_2, R^2 = H$

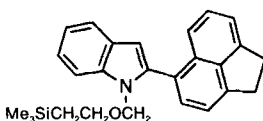
10 $R^1 = Me, R^2 = H$

11 $R^1 = H, R^2 = MeO$

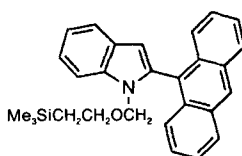
12 $R^1 = H, R^2 = AcOH$



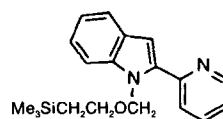
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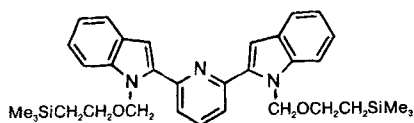
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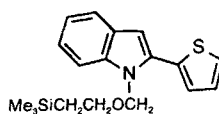
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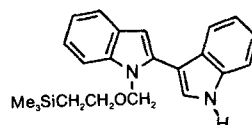
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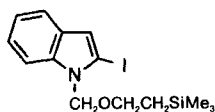
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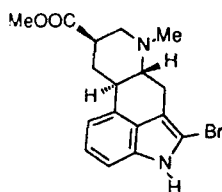
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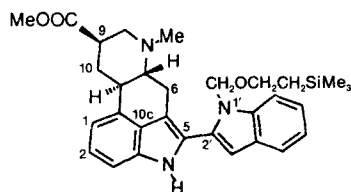
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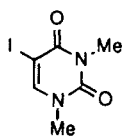
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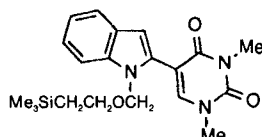
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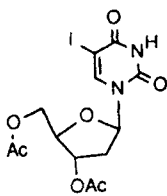
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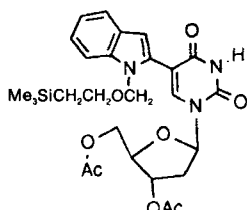
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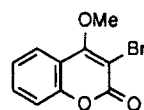
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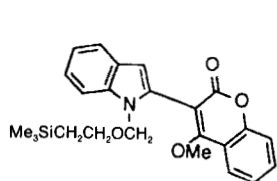
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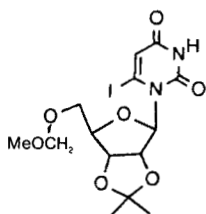
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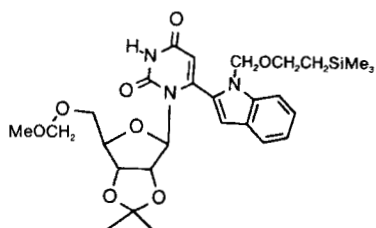
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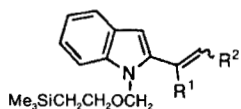
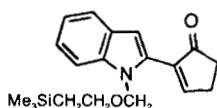
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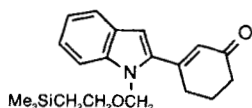
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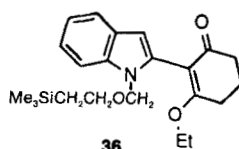
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31 $R^1 = H, R^2 = COOMe$ 32 $R^1 = H, R^2 = SiMe_3$ 33 $R^1 = COOEt, R^2 = H$ 

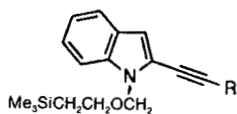
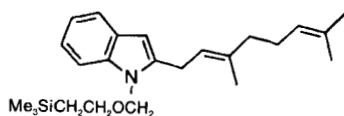
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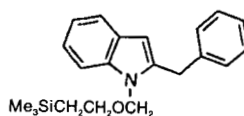
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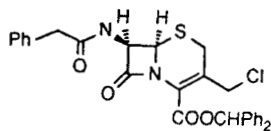
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37 $R = Me_3Si$ 38 $R = H$ 

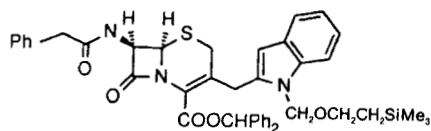
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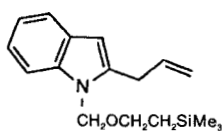
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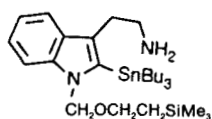
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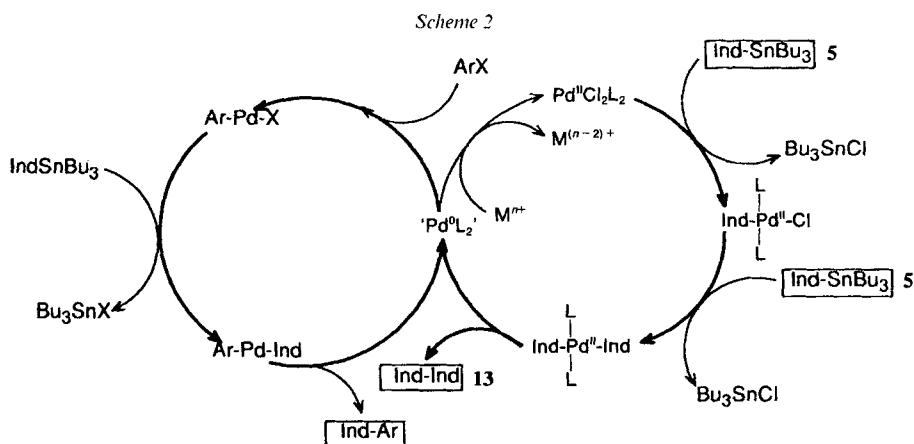
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44

remarkable improvement in the conversion **5**→**8** (*Method B*) and, unless indicated otherwise, these optimized conditions were applied throughout.

A proposal which attempts to rationalize the experimental evidence is outlined in *Scheme 2*. Under the conditions of *Method A*, the formation of the coupled product is always accompanied by the dimer **13**, and its formation was formulated as proceeding through a σ -bonded (indolyl)palladium(II) complex, $[\text{Pd}(\text{ind})_2\text{L}_2]$, formed either by a two-fold transmetalation or *via* disproportionation of the common intermediate $[\text{Pd}^{\text{II}}\text{Cl}(\text{ind})]$ [10]. Support for the mechanism outlined in *Scheme 2* comes from the observation that addition of a Cu^{II} or Ag^{I} salt as stoichiometric reoxidant to the reaction mixture of PhI and **5** (molar ratio 5:1) under the conditions of *Method A* led to the clean formation of dimer **13** as the sole product³). Although evidence for the presence of the catalytic intermediates is lacking, the catalysis of the coupling reaction by Pd^0 complexes (*Method B*) likely proceeds *via* well-established steps, *i.e.* oxidative addition of the halide on a Pd^0 complex, $[\text{PdL}_2]$, followed by transmetalation (transfer of the indol-2-yl group from **5** to $[\text{PdL}_2]$) and reductive elimination [5a]. According to *Method B*, the cross-coupling reactions tolerate a wide range of functional groups within the halide partners, as illustrated by *Entries 18, 20, and 23* (see *Table*). Also noteworthy is the fact that the presence of a bulky substituent near the reaction site does not seem to have a detrimental effect on the yield of the reaction.



As demonstrated by the entries in the *Table*, the cross-coupling of **5** was successfully achieved with a variety of vinyl and alkynyl halides. Unexpectedly, in the case of methyl 3-bromopropenoate [12]⁴) (*Entries 24 and 25*), the transfer of the vinyl group was accompanied by partial isomerization of the double bond: starting from a 7:1 (*Z*)/(*E*)-mixture, we obtained, in both cases, the coupled product **3** as a 1.5:1 (*Z*)/(*E*)-mixture; re-exposure of the starting material or the reaction product(s) to the reaction conditions

³) There are a few examples reported for Pd^{II} -induced oxidative dimerization of stannanes, see *e.g.* [11].

⁴) In contrast to [12], we obtained, under the same conditions, a 7:1 mixture of (*Z*)/(*E*)-isomers, as checked by ^1H -NMR spectra.

did not lead to isomerization in either case⁵). In contrast, (2-bromovinyl)trimethylsilane ((*Z*)/(*E*) 9:1) underwent a stereospecific coupling with stannane **5**, providing **32** with $\geq 95\%$ retention of configuration (*Entry 26*). In the case of iodo(trimethylsilyl)acetylene, the corresponding bis-protected alkyne **37** (*Entry 34*) was obtained in 88% isolated yield, and the selective removal of the Me₃Si group to yield the terminal alkyne **38** was achieved by treatment with CsF in MeCN at room temperature [14].

Finally, reaction of **5** with either geranyl bromide or (chloromethyl)cephem derivative **41** in the presence of [Pd(*tpp*)₄] (*tpp* = triphenylphosphine) in DMF at 110° (*Method B*) deserves some comment. Although the results were condition-dependent, low yields (< 30%) of the coupled products, messy reactions, and long reaction times were uniformly observed (*Entries 35* and *38*). When [Pd₂(dba)₂]·CHCl₃ (dba = dibenzalacetone) was used as catalyst, in the presence of tris(fur-2-yl)phosphine as ligand in THF (*Farina's* protocol; *Method C*) [15], however, geranyl bromide reacted with **5** in 75% yield to the 2-prenylated indole **39** (*Entry 36*). Similarly, **41** coupled cleanly under these conditions, leading to **42** (95%; *Entry 39*), in spite of the sensitive functionalities of **41**, generally not compatible with group-IA and -IIA organometallics. These couplings highlight the versatility of stannane **5**.

Conclusions. – The synthesis of 2-substituted indoles has been significantly generalized by the use of organotin technology. The protected tributyl(indol-2-yl)stannane **5**, easily prepared from 1-{[2-(trimethylsilyl)ethoxy]methyl}-1*H*-indole (**6**), undergoes a generally efficient cross-coupling with organic halides (aryl, heteroaryl, vinyl, alkynyl, and allyl). The experimental procedures are simple, conditions are relatively mild, isolation of the pure products is straightforward: these features compare favourably with those of the recently described related approaches [16]. Moreover, as the Me₃SiCH₂CH₂OCH₂ group is stable over a wide pH range and can be removed under highly selective deprotection conditions, employment of this protecting group can be warmly recommended. We are pursuing further extensions of stannylation of indole derivatives and will report later additional findings on 2-(tributylstannyl)-1-{[2-(trimethylsilyl)ethoxy]methyl}tryptamine (**44**).

Experimental Part

General. All operations were carried out under dry, O₂-free N₂. TLC: Detection by fluorescence quenching (254 or 365 nm) or with cerium(IV) ammonium sulfate (1% in 85% H₃PO₄). IR Spectra (CHCl₃): *Perkin-Elmer-681* spectrophotometer; in cm⁻¹. ¹H- and ¹³C-NMR Spectra (CDCl₃): *Bruker WP-80* or *CPX-300*, unless otherwise specified; chemical shifts δ in ppm rel. to MeSi (= 0 ppm), coupling constants *J* in Hz. ¹¹⁹Sn-NMR Spectra (CDCl₃): *Varian XL-200* (74.54 MHz), δ is referred to Me₄Sn (70 eV), HR-MS (*R* = 5000), and FAB-MS (positive mode, glycerol matrix): *VG-7070-EQ-HF* instrument, *m/z* (%).

2-(Tributylstannyl)-1-{[2-(trimethylsilyl)ethoxy]methyl}-1*H*-indole (**5**). To a soln. of 1-{[2-(trimethylsilyl)ethoxy]methyl}-1*H*-indole (**6**; 2.0 mmol) in dry 1,2-dimethoxyethane (5 ml) under N₂ at -10° was added 1.6M BuLi/hexane (1.5 ml), dropwise within 10 min. After 10 min stirring at -10°, the resulting orange soln. was cooled to -20° and treated with Bu₃SnCl (1.3 mmol). The mixture was warmed to 0° within 20 min under stirring and then poured into sat. aq. NH₄Cl soln. The mixture was extracted with Et₂O (2 × 20 ml), the combined org. extract dried (MgSO₄) and evaporated, and the residue purified by filtration on neutral alumina (hexane): pure **5** (88%).

⁵⁾ The same observation was reported for similar Pd-catalyzed reactions [13].

Colourless thick oil, $R_f(\text{Et}_2\text{O}/\text{hexane } 1:100)$ 0.29. $^1\text{H-NMR}$ (80 MHz): -0.06 (s, Me_3Si); 0.81 – 1.92 (overlapped signals, 29 H, CH_2Si , Bu_3Sn); 3.45 (dd, $J = 7.8, 8.8$, CH_2O); 5.43 (s, NCH_2O); 6.64 (d, $J = 0.8$, $\text{H-C}(3)$); 7.11 – 7.70 (overlapped signals, $\text{H-C}(4)$, $\text{H-C}(5)$, $\text{H-C}(6)$, $\text{H-C}(7)$). $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3 ; multiplicities from APT spectra): -1.43 (q, Me_3Si); 10.48 (t, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 13.69 (q, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 17.94 (t, CH_2Si); 27.39 (t, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 20.09 (t, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 65.48 (t, CH_2O); 76.22 (t, OCH_2N); 109.32 (d, $\text{C}(3)$); 113.81 (d, $\text{C}(8)$); 119.54 (d, $\text{C}(7)$); 119.93 (d, $\text{C}(6)$); 121.46 (d, $\text{C}(5)$); 129.65 (s, $\text{C}(2)$); 139.89 (s, $\text{C}(4)$); 141.87 (s, $\text{C}(9)$).

General Procedure, Method A. The yellow soln. of $[\text{PdCl}_2(\text{MeCN})_2]$ (0.1 mmol) in dry DMF (5 ml) was degassed 3 times by evacuating to 10 Torr and flushing with N_2 . Under a stream of N_2 , the halide (1.3 mmol) and neat stannane **5** (1.0 mmol) were then added ($\rightarrow$ black upon addition of **5**). After stirring for the reported time at r.t. (TLC monitoring of the stannane), the mixture was transferred to a separatory funnel with the aid of 3 ml of H_2O and extracted with Et_2O (2×20 ml). The combined Et_2O extract washed with H_2O (1×10 ml) and brine (1×10 ml), dried (Na_2SO_4), and evaporated and the residue purified by column chromatography (silica gel).

General Procedure, Method B. To a dry and degassed soln. of $[\text{Pd}(\text{tpp})_4]$ (0.01 mmol) and halide (1.3 mmol) in DMF (5 ml) was added neat stannane **5** (1.0 mmol) with a syringe. The mixture was heated at 110° in an oil bath with stirring. After the reaction was complete (TLC monitoring), this mixture was cooled to r.t., added to 20 ml of H_2O and extracted with Et_2O (2×15 ml). The combined org. layers were washed with brine and dried. The coupled product was isolated by flash chromatography (silica gel).

General Procedure, Method C. Dry THF (5 ml) was degassed with N_2 . Under a stream of N_2 , tri(fur-2-yl)phosphine (0.02 mmol) and $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ (0.01 mmol) were added. The resulting yellow soln. was treated with the halide (1.3 mmol) and, after 5 min, with neat stannane **5** (1.0 mmol). The soln. was refluxed until the reaction was complete (TLC). The mixture was evaporated and the black residue chromatographed (silica gel).

2-Phenyl-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (8). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:20)$ 0.29. $^1\text{H-NMR}$ (80 MHz): -0.02 (s, Me_3Si); 0.90 (dd, $J = 7.8, 8.7$, CH_2Si); 3.53 (dd, $J = 7.8, 8.7$, CH_2O); 5.49 (s, NCH_2O); 6.62 (d, $J = 0.8$, $\text{H-C}(3)$); 7.10 – 7.80 (9 H, overlapped arom. H). EI-MS: 323 (M^+), 265, 250, 206, 193, 178, 165, 103, 73 (100).

2-(2'-Nitrophenyl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (9). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:10)$ 0.08. $^1\text{H-NMR}$ (300 MHz): -0.10 (s, Me_3Si); 0.81 (t, $J = 8.2$, CH_2Si); 3.50 (t, $J = 8.2$, CH_2O); 5.30 (s, NCH_2O); 6.52 (s, $\text{H-C}(3)$); 7.16 (br. t, $J = 7.4$, $\text{H-C}(5)$); 7.28 (br. t, $J = 7.4$, $\text{H-C}(6)$); 7.52 (br. d, $J = 7.4$, $\text{H-C}(7)$); 7.14 – 7.72 (overlapped signals, $\text{H-C}(4)$, $\text{H-C}(4')$, $\text{H-C}(5')$, $\text{H-C}(6')$); 8.02 (br. d, $J = 7.9$, $\text{H-C}(3')$).

2-(2'-Methylphenyl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (10). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:20)$ 0.30. $^1\text{H-NMR}$ (80 MHz, CDCl_3): -0.08 (s, Me_3Si); 0.73 (dd, $J = 7.8, 8.7$, CH_2Si); 2.21 (s, Me); 3.26 (dd, $J = 7.8, 8.7$, CH_2O); 5.38 (s, NCH_2O); 6.43 (d, $J = 0.8$, $\text{H-C}(3)$); 7.11 – 7.80 (8 H, overlapped arom. H).

2-(4'-Methoxyphenyl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (11). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:20)$ 0.27. $^1\text{H-NMR}$ (300 MHz): -0.06 (s, Me_3Si); 0.87 (t, $J = 8.1$, CH_2Si); 3.50 (t, $J = 8.1$, CH_2O); 3.86 (s, MeO); 5.42 (s, NCH_2O); 6.52 (br. s, $\text{HC}(3)$); 6.98 (d, $J = 8.7$, $\text{H-C}(3')$, $\text{H-C}(5')$); 7.14 (br. t, $J = 7.8$, $\text{H-C}(5)$); 7.23 (br. t, $J = 7.8$, $\text{H-C}(6)$); 7.48 (br. d, $J = 7.8$, $\text{H-C}(7)$); 7.54 (d, $J = 8.7$, $\text{H-C}(2')$, $\text{H-C}(6')$); 7.59 (br. d, $J = 7.8$, $\text{H-C}(4)$).

2-(4'-Acetylphenyl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (12). $R_f(\text{Et}_2\text{O}/\text{hexane } 3:10)$ 0.29. $^1\text{H-NMR}$ (300 MHz): -0.08 (s, Me_3Si); 0.92 (t, $J = 8.0$, CH_2Si); 2.67 (s, MeCO); 3.58 (t, $J = 8.0$, CH_2O); 5.47 (s, NCH_2O); 6.70 (br. s, $\text{H-C}(3)$); 7.17 (br. t, $J = 7.9$, $\text{H-C}(5)$); 7.29 (br. t, $J = 7.9$, $\text{H-C}(6)$); 7.52 (br. d, $J = 7.9$, $\text{H-C}(7)$); 7.61 (br. d, $J = 7.9$, $\text{H-C}(4)$); 7.77 (d, $J = 8.2$, $\text{H-C}(2')$, $\text{H-C}(6')$); 8.04 (d, $J = 8.2$, $\text{H-C}(3')$, $\text{H-C}(5')$).

1,1'-Bis- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -2,2'-bi(1H-indole) (13). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:20)$ 0.36. $^1\text{H-NMR}$ (80 MHz): -0.08 (s, 2 Me_3Si); 0.85 (dd, $J = 7.9, 8.9$, 2 CH_2O); 5.43 (s, 2 NCH_2O); 6.82 (d, $J = 0.8$, 2 H, $\text{H-C}(3)$); 7.11 – 7.39 (overlapped signals, 4 H, $\text{H-C}(6)$, $\text{H-C}(5)$); 7.45 – 7.75 (overlapped signals, 4 H, $\text{H-C}(4)$, $\text{H-C}(7)$). EI-MS: 492 (M^+), 375, 333, 273, 259, 244, 202, 158, 147, 130, 117, 103 (100).

2-(1',2'-Dihydroacenaphthylene-5'-yl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (14). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:30)$ 0.18. $^1\text{H-NMR}$ (300 MHz): -0.22 (s, Me_3Si); 0.62 (t, $J = 8.2$, CH_2Si); 3.13 (t, $J = 8.2$, CH_2O); 3.34 (s, 2 $\text{H-C}(1')$, 2 $\text{H-C}(2')$); 5.34 (s, OCH_2N); 6.61 (s, $\text{H-C}(3)$); 7.17 (br. t, $J = 7.4$, $\text{H-C}(5)$); 7.20 – 7.60 (6 H, overlapped arom. H); 7.64 (br. d, $J = 7.4$, $\text{H-C}(4)$).

2-(Anthracen-9'-yl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (15). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:100)$ 0.14. $^1\text{H-NMR}$ (80 MHz): -0.27 (s, Me_3Si); 0.50 (dd, $J = 7.5, 9.0$, CH_2Si); 2.95 (dd, $J = 7.5, 9.0$, CH_2O); 5.12 (s, NCH_2O); 6.78 (d, $J = 0.5$, $\text{H-C}(3)$); 7.11 – 8.20 (12 H, overlapped arom. H); 8.59 (br. s, $\text{H-C}(10')$).

2-(Pyrid-2'-yl)-1- $\{[2-(\text{trimethylsilyl})\text{ethoxy}]\text{methyl}\}$ -1H-indole (16). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:10)$ 0.14. $^1\text{H-NMR}$ (300 MHz): -0.17 (s, Me_3Si); 0.81 (t, $J = 8.4$, CH_2Si); 3.43 (t, $J = 8.4$, CH_2O); 6.07 (s, NCH_2O); 6.96 (s, $\text{H-C}(3)$); 7.18 (br. t, $J = 7.4$, $\text{H-C}(5)$); 7.26 (overlapped signal, $\text{HC}(5')$); 7.32 (br. t, $J = 7.4$, $\text{H-C}(6)$); 7.60 (br. d, $J = 7.4$, $\text{H-C}(7)$); 7.67 (br. d, $J = 7.4$, $\text{H-C}(4)$); 7.75 (br. d, $J = 4.9$, $\text{H-C}(3')$); 7.78 (br. t, $J = 4.9$, $\text{H-C}(4')$); 8.70 (br. d, $J = 4.9$, $\text{H-C}(3')$).

2,2'-(Pyridine-2,6-diyl)-1,1'-{2-(trimethylsilyl)ethoxy}methyl}bi(1H-indol) (17). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:20)$ 0.09. $^1\text{H-NMR}$ (300 MHz): -0.18 (s, 2 Me_3Si); 0.74 (t, $J = 8.0$, 2 CH_2Si); 3.38 (t, $J = 8.2$, 2 CH_2O); 6.03 (s, 2 OCH_2N); 7.02 (s, 2 H, $\text{H-C}(3)$); 7.19 (dt, $J = 7.8$, 1.2, 2 H, $\text{H-C}(5)$); 7.31 (dt, $J = 7.8$, 1.2, 2 H, $\text{H-C}(6)$); 7.55 (br. d, $J = 7.8$, 2 H, $\text{H-C}(7)$); 7.68 (br. d, $J = 7.8$, 2 H, $\text{H-C}(4)$); 7.77 (br. d, $J = 7.5$, $\text{H-C}(3')$, $\text{H-C}(5')$ of py); 7.88 (br. d, $J = 7.5$, $\text{H-C}(4)$ of py).

2-(Thiophen-2'-yl)-1'-{2-(trimethylsilyl)ethoxy}methyl}-1H-indole (18). $R_f(\text{Et}_2\text{O}/\text{hexane } 1:20)$ 0.29. $^1\text{H-NMR}$ (300 MHz): -0.04 (s, Me_3Si); 0.92 (t, $J = 8$, CH_2Si); 3.56 (t, $J = 8$, CH_2O); 5.57 (s, NCH_2O); 6.72 (br. s, $\text{H-C}(3)$); 7.13 (br. s, $J = 4.5$, $\text{H-C}(5')$); 7.14 (br. t, $\text{H-C}(5)$); 7.26 (br. t, $J = 7.5$, $\text{H-C}(6)$); 7.40 (br. d, $J = 4.5$, $\text{H-C}(3')$); 7.43 (br. t, $J = 4.5$, $\text{H-C}(4')$); 7.48 (br. d, $J = 7.5$, $\text{H-C}(7)$); 7.62 (br. d, $J = 7.5$, $\text{H-C}(4)$).

1'-{2-(Trimethylsilyl)ethoxy}methyl}-2,3'-bi(1H-indole) (19). $R_f(\text{CH}_2\text{Cl}_2/\text{hexane } 2:5)$ 0.27. $^1\text{H-NMR}$ (300 MHz): -0.06 (s, Me_3Si); 0.90 (t, $J = 8.5$, CH_2Si); 3.55 (t, $J = 8.5$, CH_2O); 5.51 (s, OCH_2N); 6.76 (d, $J = 0.8$, $\text{H-C}(3)$); 7.19 (dt, $J = 0.5$, 8.0, $\text{H-C}(5)$); 7.23 (dt, $J = 0.5$, 8.0, $\text{H-C}(5')$); 7.24 (s, $\text{H-C}(2')$); 7.28 (dt, $J = 0.5$, 8.0, $\text{H-C}(6)$); 7.30 (dt, $J = 0.5$, 8.0, $\text{H-C}(6')$); 7.48 (br. d, $J = 8.0$, $\text{H-C}(7)$); 7.55 (br. d, $J = 8.0$, $\text{H-C}(7')$); 7.68 (br. d, $J = 8.0$, $\text{H-C}(4)$); 7.87 (br. d, $J = 8.0$, $\text{H-C}(4')$).

Methyl 4,6,6a,7,8,9,10,10a-Octahydro-7-methyl-5-{1'-{2-(trimethylsilyl)ethoxy}methyl}-1H-indol-2'-yl}-indolo[4,3-fg]quinoline (22). $R_f(\text{CHCl}_3/\text{MeOH } 25:1)$ 0.48. $^1\text{H-NMR}$ (300 MHz): 0.01 (s, Me_3Si); 1.10 (m, CH_2Si); 1.60 (ddd, $J = 14.0$, 14.0, 14.0, $\text{H}_\beta\text{-C}(10)$); 2.21 (ddd, $J = 4.1$, 11.0, 11.0, $\text{H-C}(6a)$); 2.36 (dd, $J = 11.6$, 11.6, $\text{H}_\beta\text{-C}(8)$); 2.50 (s, MeN); 2.87 (dd, $J = 15.4$, 11.0, $\text{H}_\alpha\text{-C}(6)$); 3.10 (m, $\text{H-C}(9)$, $\text{H-C}(10a)$, $\text{H}_\alpha\text{-C}(10)$); 3.28 (dd, $J = 11.6$, 5.2, $\text{H}_\alpha\text{-C}(8)$); 3.54 (dd, $J = 15.4$, 4.1, $\text{H}_\beta\text{-C}(6)$); 3.75 (s, COOMe); 3.82 (dt, $J = 5.1$, 7.5, CH_2O); 5.58 (s, OCH_2N); 6.78 (s, $\text{H-C}(3')$); 6.98 (br. d, $J = 6.0$, $\text{H-C}(1)$); $7.15\text{--}7.31$ (4 H, overlapped arom. H); 7.47 (br. d, $J = 7.7$, $\text{H-C}(7')$); 7.68 (br. d, $J = 7.7$, $\text{H-C}(4')$). $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3 ; multiplicities from APT spectra): -0.56 (q, Me_3Si); 18.80 (t, CH_2Si); 24.34 (t, $\text{C}(6)$); 31.10 (t, $\text{C}(8)$); 40.81 (d, $\text{C}(9)$); 42.12 (d, $\text{C}(10a)$); 43.90 (q, MeN); 52.5 (q, COOMe); 59.28 (t, $\text{C}(10a)$); 67.36 (t, CH_2O); 67.15 (d, $\text{C}(6a)$); 73.40 (t, OCH_2N); 105.10 (d, $\text{C}(3')$); 109.49 (d, $\text{C}(3)$, $\text{C}(7')$); 112.45 (s, $\text{C}(5a)$); 114.69 (d, $\text{C}(1)$); 121.34 (d, $\text{C}(5')$); 121.44 (d, $\text{C}(6')$); 123.85 (d, $\text{C}(2)$); 124.3 (d, $\text{C}(4')$); 127.62 (s, $\text{C}(3a)$); 128.84 (s, $\text{C}(5)$); 133.41 (s, $\text{C}(10c)$, $\text{C}(2')$); 134.10 (s, $\text{C}(10b)$, $\text{C}(3'a)$); 138.72 (s, $\text{C}(7'a)$); 174.9 (s, COOMe).

1,3-Dimethyl-5-{1'-{2-(trimethylsilyl)ethoxy}methyl}-1'H-indol-2'-yl}pyrimidine-2,4(1H,3H)-dione (24). $R_f(\text{AcOEt}/\text{hexane } 1:2)$ 0.34. $^1\text{H-NMR}$ (300 MHz): -0.12 (s, Me_3Si); 0.80 (t, $J = 8.2$, CH_2Si); 3.38 (s, MeN); 3.42 (s, MeN); 3.43 (t, $J = 8.2$, CH_2O); 5.38 (s, OCH_2N); 5.56 (br. s, $\text{H-C}(3)$); 7.08 (br. t, $J = 7.8$, $\text{H-C}(5)$); 7.19 (br. t, $J = 7.8$, $\text{H-C}(6)$); 7.41 (br. d, $J = 7.8$, $\text{H-C}(7)$); 7.54 (br. d, $J = 7.8$, $\text{H-C}(4)$); 7.55 (s, $\text{H-C}(6')$).

3',5'-Di-O-acetyl-2'-deoxy-5-{1'-{2-(trimethylsilyl)ethoxy}methyl}-1''H-indol-2''-yl}uridine (26). $R_f(\text{CHCl}_3/\text{MeOH } 200:1)$ 0.48. $^1\text{H-NMR}$ (300 MHz): -0.01 (s, Me_3Si); 0.83 (t, $J = 8.0$, CH_2Si); 1.80 (s, AcO); 2.09 (s, AcO); 2.28 (dd, $J = 14.1$, 7.0, $\text{H}_\beta\text{-C}(2')$); 2.51 (br. dd, $J = 14.1$, 5.4, $\text{H}_\alpha\text{-C}(2')$); 3.44 (t, $J = 8.0$, CH_2O); 4.25 (overlapped signals, 2 $\text{H-C}(5')$, $\text{H-C}(4')$); 5.20 (2d, $J = 5.4$, $\text{H-C}(3')$); 5.45 (s, OCH_2N); 6.38 (br. d, $J = 7.0$, $\text{H-C}(1')$); 6.60 (br. s, $\text{H-C}(3'')$); 7.11 (br. t, $J = 7.5$, $\text{H-C}(5'')$); 7.22 (br. t, $J = 7.5$, $\text{H-C}(6'')$); 7.43 (br. d, $J = 7.5$, $\text{H-C}(7'')$); 7.55 (br. d, $J = 7.5$, $\text{H-C}(4'')$); 7.89 (s, $\text{H-C}(6)$); 9.46 (br. s, NH).

4-Methoxy-3-{1'-{2-(trimethylsilyl)ethoxy}methyl}-1'H-indol-2'-yl}-2H-1-benzopyran-2-one (28). $R_f(\text{AcOEt}/\text{hexane } 1:3)$ 0.39. $^1\text{H-NMR}$ (300 MHz): -0.09 (s, Me_3Si); 0.91 (t, $J = 7.5$, CH_2Si); 3.53 (t, $J = 7.5$, CH_2O); 3.73 (s, MeO); 5.45 (AB, $J = 11.0$, OCH_2N); 6.62 (br. s, $\text{H-C}(3')$); 7.14 (br. t, $J = 7.8$, $\text{H-C}(5')$); 7.26 (br. t, $J = 7.8$, $\text{H-C}(6')$); 7.31 (br. t, $J = 8.2$, $\text{H-C}(7)$); 7.36 (br. d, $J = 8.2$, $\text{H-C}(8)$); 7.49 (br. d, $J = 7.8$, $\text{H-C}(7')$); 7.59 (br. t, $J = 8.2$, $\text{H-C}(6)$); 7.61 (br. d, $J = 7.8$, $\text{H-C}(4')$); 7.92 (br. d, $J = 8.2$, $\text{H-C}(5)$).

2',3'-O-Isopropylidene-5'-O-(methoxymethyl)-6-{1''-{2-(trimethylsilyl)ethoxy}methyl}-1''H-indol-2''-yl}-uridine (30). $R_f(\text{AcOEt}/\text{hexane } 2:1)$ 0.36. $^1\text{H-NMR}$ (300 MHz): 0.11 (s, Me_3Si); 0.83 (t, $J = 8.0$, CH_2Si); 1.24 (s, MeC); 1.32 (s, MeC); 3.37 (t, $J = 8.0$, CH_2O); 3.74 (s, MeO); 3.75 (m, 2 $\text{H-C}(5')$); 4.10 (dt, $J = 6.4$, 4.4, $\text{H-C}(4')$); 4.65 (s, OCH_2O); 4.84 (dd, $J = 6.4$, 4.4, $\text{H-C}(3')$); 5.19 (d, $J = 6.4$, $\text{H-C}(2')$); 5.45 (s, $\text{H-C}(5)$); 5.50 (s, OCH_2N); 5.87 (s, $\text{H-C}(1')$); 6.85 (br. s, $\text{H-C}(3'')$); 7.22 (br. t, $J = 7.9$, $\text{H-C}(5'')$); 7.35 (br. t, $J = 7.9$, $\text{H-C}(6'')$); 7.52 (br. d, $J = 7.9$, $\text{H-C}(7'')$); 7.68 (br. d, $J = 7.9$, $\text{H-C}(4'')$); 9.37 (br. s, NH). FAB-MS: 825.

Methyl (E)-3-{1'-{2-(Trimethylsilyl)ethoxy}methyl}-1'H-indol-2'-yl}prop-2-enoate ((E)-31). $R_f(\text{CH}_2\text{Cl}_2/\text{hexane } 1:2)$ 0.24. IR: 1710, 1635. $^1\text{H-NMR}$ (300 MHz): -0.12 (s, Me_3Si); 0.84 (t, $J = 8.0$, CH_2Si); 3.41 (t, $J = 8.2$, CH_2O); 3.77 (s, COOMe); 5.54 (s, OCH_2N); 6.49 (d, $J = 15.9$, $\text{H-C}(2')$); 6.94 (br. s, $\text{H-C}(3')$); 7.09 (br. t, $J = 7.8$, $\text{H-C}(5')$); 7.23 (br. t, $J = 7.8$, $\text{H-C}(6')$); 7.40 (br. d, $J = 7.8$, $\text{H-C}(7')$); 7.56 (br. d, $J = 7.8$, $\text{H-C}(4')$); 7.81 (d, $J = 15.9$, $\text{H-C}(3)$). EI-MS: 331 (M^+), 301, 273, 258, 242, 214, 169, 154, 111, 73 (100).

Methyl (Z)-3-{1'-{2-(Trimethylsilyl)ethoxy}methyl}-1'H-indol-2'-yl}prop-2-enoate ((Z)-31). $R_f(\text{CH}_2\text{Cl}_2/\text{hexane } 1:2)$ 0.36. IR: 1718, 1625. $^1\text{H-NMR}$ (300 MHz): -0.18 (s, Me_3Si); 0.81 (t, $J = 8.1$, CH_2Si); 3.44 (t, $J = 8.1$, CH_2O); 3.73 (s, COOMe); 5.51 (s, OCH_2N); 5.94 (d, $J = 12.8$, $\text{H-C}(2)$); 7.07 (br. t, $J = 7.8$, $\text{H-C}(5')$); 7.09 (d,

$J = 12.8$, H-C(3)); 7.22 (br. t , $J = 7.8$, H-C(6')); 7.28 (br. d , $J = 7.8$, H-C(7')); 7.60 (br. d , $J = 7.8$, H-C(4')); 7.70 (br. s , H-C(3')). EI-MS: 331 (M^+), 301, 273, 258, 247, 214, 169, 73 (100).

(E)-2-[2'-(Trimethylsilyl)ethoxy]methyl-1-[2-(trimethylsilyl)ethoxy]methyl-1-H-indole (32). R_f (Et₂O/hexane 1:100) 0.17. ¹H-NMR (300 MHz): -0.09 (s , Me₃Si); 0.16 (s , Me₃Si); 0.86 (t , $J = 8.0$, CH₂Si); 3.49 (t , $J = 8.2$, CH₂O); 5.53 (s , OCH₂N); 6.59 (d , $J = 19.0$, H-C(2')); 6.74 (br. s , H-C(3)); 7.00 (d , $J = 19.0$, H-C(1')); 7.08 (br. t , $J = 7.9$, H-C(5)); 7.18 (br. t , $J = 7.9$, H-C(6)); 7.40 (br. d , $J = 7.9$, H-C(7)); 7.55 (br. d , $J = 7.9$, H-C(4)).

Ethyl 2-[1'-{2-(Trimethylsilyl)ethoxy}methyl]-1'-H-indol-2'-yl}prop-2-enoate (33). R_f (CH₂Cl₂/hexane 1:1) 0.39. IR: 1730. ¹H-NMR (300 MHz): -0.09 (s , Me₃Si); 0.83 (t , $J = 8.2$, CH₂Si); 1.29 (t , $J = 7.2$, MeCH₂O); 3.39 (t , $J = 8.2$, CH₂O); 4.25 (q , $J = 7.2$, MeCH₂O); 5.38 (s , OCH₂N); 6.09 (d , $J = 1.0$, 1 H-C(3)); 6.56 (br. s , H-C(3')); 6.61 (d , $J = 1.0$, 1 H-C(3)); 7.12 (br. t , $J = 7.9$, H-C(5')); 7.23 (br. t , $J = 7.9$, H-C(6')); 7.46 (br. d , $J = 7.9$, H-C(7')); 7.58 (br. d , $J = 7.9$, H-C(4')).

2-[1'-{2-(Trimethylsilyl)ethoxy}methyl]-1'-H-indol-2'-yl}cyclopent-2-en-1-one (34). R_f (CH₂Cl₂) 0.46. ¹H-NMR (300 MHz): -0.08 (s , Me₃Si); 0.97 (t , $J = 8.2$, CH₂Si); 2.59 (t , $J = 3.5$, 2 H-C(5')); 2.79 (dt , $J = 1.0$, 3.5, 2 H-C(4)); 3.54 (t , $J = 8.2$, CH₂O); 5.42 (s , OCH₂N); 7.03 (br. s , H-C(3')); 7.11 (br. t , $J = 8.0$, H-C(5')); 7.22 (br. t , $J = 8.0$, H-C(6')); 7.42 (br. d , $J = 8.0$, H-C(7')); 7.61 (br. d , $J = 8.0$, H-C(4')); 8.06 (t , $J = 1.0$, H-C(3)).

3-[1'-{2-(Trimethylsilyl)ethoxy}methyl]-1'-H-indol-2'-yl}cyclohex-2-en-1-one (35). R_f (Et₂O/hexane 1:20) 0.05. IR: 1655, 1598. ¹H-NMR (80 MHz): -0.09 (s , Me₃Si); 0.91 (dd , $J = 7.8$, 8.7, CH₂Si); 2.08 (m , 2 H-C(5)); 2.67 (m , 2 H-C(4), 2 H-C(6)); 3.50 (dd , $J = 7.8$, 8.7, CH₂O); 5.50 (s , OCH₂N); 6.50 (s , H-C(2)); 6.83 (s , H-C(3')); 7.01–7.7 (4 H, overlapped arom. H).

3-Ethoxy-2-[1'-{2-(trimethylsilyl)ethoxy}methyl]-1'-H-indol-2'-yl}cyclohex-2-en-1-one (36). R_f (AcOEt/CH₂Cl₂ 1:9) 0.21. ¹H-NMR (300 MHz): -0.01 (s , Me₃Si); 0.79 (t , $J = 8.2$, CH₂Si); 1.14 (t , $J = 7.0$, MeCH₂O); 2.14 (tt , $J = 6.5$, 6.5, 2 H-C(5)); 2.50 (t , $J = 6.5$, 2 H-C(6)); 2.70 (t , $J = 6.5$, 2 H-C(4)); 3.34 (t , $J = 8.2$, CH₂O); 3.90, 3.96 (2 q , $J = 7.0$, 7.0, MeCH₂O, diastereoisotopic); 5.23 (AB , $J = 9.0$, OCH₂N); 6.31 (br. s , H-C(3')); 7.07 (br. t , $J = 7.8$, H-C(5')); 7.16 (br. t , $J = 7.8$, H-C(6')); 7.45 (br. d , $J = 7.8$, H-C(7')); 7.53 (br. d , $J = 7.8$, H-C(4')).

1-[2-(Trimethylsilyl)ethoxy]methyl-2-[2-(trimethylsilyl)ethynyl]-1-H-indole (37). R_f (Et₂O/hexane 1:100) 0.17. ¹H-NMR (300 MHz): -0.09 (s , Me₃Si); 0.27 (s , Me₃Si); 0.88 (t , $J = 8.1$, CH₂Si); 3.50 (t , $J = 8.1$, CH₂O); 5.61 (s , OCH₂N); 6.77 (s , H-C(3)); 7.12 (br. t , $J = 7.9$, H-C(5)); 7.26 (br. t , $J = 7.9$, H-C(6)); 7.46 (br. d , $J = 7.9$, H-C(7)); 7.56 (br. d , $J = 7.9$, H-C(4)).

2-Ethynyl-1-[2-(trimethylsilyl)ethoxy]methyl-1-H-indole (38). R_f (Et₂O/hexane 1:100) 0.06. ¹H-NMR (300 MHz): -0.09 (Me₃Si); 0.86 (t , $J = 7.4$, CH₂Si); 2.02 (s , C≡CH); 3.44 (t , $J = 7.4$, CH₂O); 5.47 (s , OCH₂N); 6.50 (d , $J = 1.5$, H-C(3)); 7.12 (br. t , $J = 8.0$, H-C(5)); 7.15 (br. t , $J = 8.0$, H-C(6)); 7.45 (br. d , $J = 8.0$, H-C(7)); 7.60 (br. d , $J = 8.0$, H-C(4)).

2-[2E]-3',7'-Dimethylocta-2',6'-dien-1'-yl]-1-[2-(trimethylsilyl)ethoxy]methyl-1-H-indole (39). R_f (i-Pr₂O/hexane 1:25) 0.24. ¹H-NMR (300 MHz): -0.05 (s , Me₃Si); 0.89 (t , $J = 7.9$, CH₂Si); 1.27 (s , Me); 1.62 (s , Me); 1.72 (s , Me); 2.12 (m , 2 H-C(4'), 2 H-C(5')); 3.50 (t , $J = 7.9$, CH₂O); 3.51 (br. d , $J = 7.0$, 2 H-C(1')); 5.13 (br. t , $J = 6.8$, H-C(6')); 5.40 (br. t , $J = 7.0$, H-C(2')); 5.45 (s , OCH₂N); 6.29 (br. s , H-C(3)); 7.08 (br. t , $J = 7.9$, H-C(5)); 7.17 (br. t , $J = 7.9$, H-C(6)); 7.41 (br. d , $J = 7.9$, H-C(7)); 7.52 (br. d , $J = 7.9$, H-C(4)).

2-Benzyl-1-[2-(trimethylsilyl)ethoxy]methyl-1-H-indole (40). R_f (Et₂O/hexane 1:10) 0.40. ¹H-NMR (300 MHz): -0.07 (s , Me₃Si); 0.88 (t , $J = 8.2$, CH₂Si); 3.41 (t , $J = 8.1$, CH₂O); 4.21 (br. s , PhCH₂); 5.36 (s , OCH₂N); 6.27 (br. s , H-C(3)); 7.10 (br. t , $J = 7.6$, H-C(5)); 7.19 (br. t , $J = 7.9$, H-C(6)); 7.27 (m , PhCH₂); 7.41 (br. d , $J = 7.9$, H-C(7)); 7.54 (br. d , $J = 7.9$, H-C(4)).

Diphenylmethyl 8-Oxo-7-[(phenylacetyl)amino]-3-[[1'-{2-(trimethylsilyl)ethoxy}methyl]-1'-H-indol-2'-yl]methyl]-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylate (42). R_f (AcOEt/hexane 1:2) 0.27. ¹H-NMR (300 MHz): -0.01 (s , Me₃Si); 0.79 (t , $J = 8.2$, CH₂Si); 3.32 (AB , $J = 16.0$, 2 H-C(4)); 3.38 (t , $J = 7.9$, CH₂O); 3.64 (AB , $J = 14.2$, CH₂CO); 3.98 (AB , $J = 15.8$, CH₂C(3)); 4.97 (d , $J = 4.6$, H-C(6')); 5.23 (AB , $J = 11.0$, OCH₂N); 5.84 (dd , $J = 4.6$, 8.4, H-C(7)); 6.17 (d , $J = 8.4$, NH); 6.25 (s , H-C(3')); 6.93 (s , Ph₂CH); 7.11 (br. t , $J = 7.2$, H-C(5')); 7.20–7.35 (16 H, overlapped arom. H); 7.37 (br. d , $J = 7.2$, H-C(7')); 7.56 (br. d , $J = 7.2$, H-C(4')). EI-MS: 743 (M^+), 625, 458, (100), 414, 357, 283, 241.

2-(Prop-2-en-1'-yl)-1-[2-(trimethylsilyl)ethoxy]methyl-1-H-indole (43). R_f (i-Pr₂O/hexane 1:25) 0.24. ¹H-NMR (300 MHz): -0.06 (s , Me₃Si); 0.89 (t , $J = 7.9$, CH₂Si); 3.50 (t , $J = 7.9$, CH₂O); 3.62 (br. d , $J = 6.4$, 2 H-C(1')); 5.08 (ddt , $J = 18.6$, 1.0, 1.0, 1 H-C(3')); 5.18 (ddt , $J = 10.7$, 1.0, 1.0, 1 H-C(3')); 5.46 (s , OCH₂N); 6.07 (ddt , $J = 18.6$, 10.7, 6.4, H-C(2')); 6.32 (br. s , H-C(3)); 7.10 (br. t , $J = 7.9$, H-C(5)); 7.19 (br. t , $J = 7.9$, H-C(6)); 7.42 (br. d , $J = 7.9$, H-C(7)); 7.53 (br. d , $J = 7.9$, H-C(4)).

We would like to thank *Alessandra Ghilardi* and *Dahlia Nathaniel* for their skillful assistance in the synthetic work. We are also indebted to *A. Cremonesi* for performing elemental analyses and HR-MS determinations.

REFERENCES

- [1] For an exhaustive review on indole chemistry, see R. J. Parry, J. C. Powers, K. Rush, L. R. Smith, F. Troxler, 'Indoles, Part II', in 'The Chemistry of Heterocyclic Compounds', Ed. W. J. Houlihan, Wiley-Interscience, New York, 1972.
- [2] U. Pindur, *Chimia* **1985**, 39, 264; J. E. Macor, M. E. Newman, K. Ryan, *Tetrahedron Lett.* **1989**, 30, 2509; U. Pindur, M. Eitel, *Helv. Chim. Acta* **1988**, 71, 1060; J. Bergman, B. Pelcman, *Tetrahedron* **1988**, 44, 5215; M. Eitel, U. Pindur, *J. Org. Chem.* **1990**, 55, 5368.
- [3] W. G. Bornmann, M. E. Kuehne, *J. Org. Chem.* **1992**, 57, 1752, and ref. cit. therein; J. Lévy, J. Sapi, J.-Y. Laronze, D. Royer, L. Toupet, *Synlett* **1992**, 601.
- [4] U. Pindur, M. H. Kim, *Tetrahedron Lett.* **1988**, 29, 3927.
- [5] a) J. K. Stille, *Angew. Chem. Int. Ed.* **1986**, 25, 508; *Pure Appl. Chem.* **1985**, 57, 1711; b) I. P. Beletskaya, *J. Organomet. Chem.* **1983**, 250, 551; c) for a recent review on this topic, see T. N. Mitchell, *Synlett* **1992**, 803.
- [6] V. N. Kalinin, *Synthesis* **1992**, 413; see also M. Pereyre, J. P. Quintard, A. Rahm, 'Tin in Organic Synthesis', Butterworth & Co., London, 1989.
- [7] S. Caddick, S. Joshi, *Synlett* **1992**, 805.
- [8] H. F. Hodson, D. J. Madge, D. A. Widdowson, *Synlett* **1992**, 831.
- [9] a) M. P. Edwards, A. M. Doherty, S. V. Ley, H. M. Organ, *Tetrahedron* **1986**, 42, 3723; b) T. Kline, *J. Heterocycl. Chem.* **1985**, 22, 505.
- [10] R. F. Heck, 'Palladium Reagents in Organic Synthesis', Academic Press, London, 1985.
- [11] L. S. Liebeskind, S. W. Riesinger, *Tetrahedron Lett.* **1991**, 32, 5681; G. A. Tolstikov, M. S. Miftakhov, N. A. Danilova, Y. L. Velder, L. V. Spirikhin, *Synthesis* **1989**, 8, 633; S. Kanemoto, S. Matsubara, K. Oshima, K. Utimoto, H. Nozaki, *Chem. Lett.* **1987**, 5.
- [12] E. Gryszkiewicz-Trochimowski, W. Schmidt, O. Gryszkiewicz-Trochimowski, *Bull. Soc. Chim. Fr.* **1948**, 539.
- [13] G. Palmisano, M. Santagostino, *Tetrahedron* **1993**, 49, 2533; I. N. Houpis, *Tetrahedron Lett.* **1991**, 32, 6675.
- [14] S. G. Davies, D. Pyatt, C. Thomson, *J. Organomet. Chem.* **1990**, 387, 391.
- [15] V. Farina, S. R. Baker, R. A. Benigni, S. I. Hauck, C. Sapino, *J. Org. Chem.* **1990**, 55, 5833, and ref. cit. therein.
- [16] E. Wenkert, J. M. Hanna, M. H. Leftin, E. L. Michelotti, K. T. Potts, D. Usifer, *J. Org. Chem.* **1985**, 50, 1125; A. Minato, K. Tamao, T. Hayashi, K. Suzuki, M. Kumada, *Tetrahedron Lett.* **1981**, 22, 5319; P. Vincent, J. P. Beaucourt, L. Richat, *ibid.* **1984**, 25, 201; A. Arcadi, S. Cacchi, F. Marinelli, *ibid.* **1986**, 42, 2111; M. Ishikura, M. Terashima, *J. Chem. Soc., Chem. Commun.* **1989**, 135.