Indol-2-yltributylstannane: A Versatile Reagent for 2-Substituted Indoles[1]

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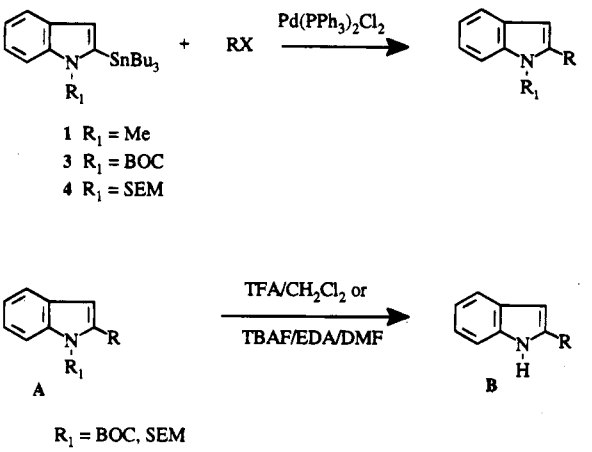
A general method for 2-substituted indoles via the palladium-catalyzed coupling of indol-2-ylstannanes is described. (*N*-Methylindol-2-yl)tributylstannane (**1**) reacts with a variety of electrophiles under very mild conditions. [*N*-*tert*-Butoxycarbonyl)indol-2-yl]tributylstannane (**3**) is much less reactive in the coupling reactions and reacts only with certain activated electrophiles. [*N*-[[(Trimethylsilyl)ethoxy]methylindol-2-yl]tributylstannane (**4**) behaves similarly to **1** and the removal of the [(trimethylsilyl)ethoxy]methyl group can be achieved with tetra-*n*-butylammonium fluoride in DMF in the presence of ethylenediamine.

The indole nucleus is prevalent in a large number of naturally occurring as well as biologically active molecules. A large number of known methods of preparation of indoles involve *de novo* construction of the indole nucleus.[2] Metalation of indoles at the 2-position has been described and has been recently utilized to a great extent in the synthesis of 2-substituted indoles.[3] The reaction of the 2-lithio species with tributyltin chloride provides indol-2-yltributylstannane in excellent yield.[4] However, to date, the scope of the use of indol-2-ylstannane in the synthesis of 2-substituted indoles has not been investigated.[5] In order to expand the structure activity–relationship of a 2-substituted indole series in one of our medicinal chemistry programs, we required a general one-step method for the preparation of 2-substituted indoles. It was envisaged that the palladium-catalyzed coupling of this reagent with common coupling partners, such as acyl, aryl, vinyl, and allyl halides and aryl and vinyl triflates, would lead to a facile method for the synthesis of a variety of 2-substituted indoles (Scheme 1) which may not be attainable by the reaction of the 2-lithioindole with respective electrophiles.[6,7] In this paper we describe the synthetic utility of indol-2-ylstannanes.

Scheme 1



(*N*-Methylindol-2-yl)tributylstannane (1). Lithiation of *N*-methylindole with *n*-butyllithium in dry THF at 0–5 °C and reaction of the resulting anion with tributyltin chloride proceeds smoothly to provide **1** in 78% yield. The stannane **1** is unstable under acidic conditions and therefore could not be purified by flash chromatography; however, it could easily be purified by distillation. The stannylindole **1** reacts with a variety of partners in the presence of 2 mol % bis(triphenylphosphine)palladium(II) dichloride (**2**) under very mild conditions to provide excellent yields of 2-substituted indoles (Table 1). All the coupling reactions are accompanied by the formation of small amounts of 2,2′-bisindole. In some cases, bisindole poses problems during purification by flash chromatography due to similar chromatographic characteristics as the desired products. The coupling with benzyl halides (entries 1 and 2, Table 1) proceeds cleanly in THF and a polar solvent, such as, HMPA is unnecessary.[8] In coupling reactions with triflates better yields were obtained in the presence of 3 equiv of lithium chloride. Arylsulfonyl chlorides (entry 9, Table 1) are poor coupling partners and provided only trace amounts

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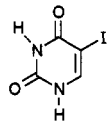
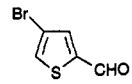
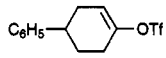
Table 1. Coupling Reactions of (*N*-Methylindol-2-yl)tributylstannane[a]

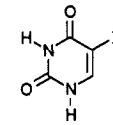
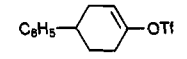
entry	RX	time (h)	% yield[b]
1	$C_6H_5CH_2Br$	1	70
2	$4\text{-}NO_2C_6H_4CH_2Br$	1	79
3	3-bromopyridine	2	70
4	$4\text{-}MeC_6H_4I$	2	82
5	$4\text{-}CNC_6H_4Br$	2	91
6	$EtOOCC_6H_4I$	2	89
7		20	60
8		2	89
9	$4\text{-}MeOC_6H_4SO_2Cl$	0.5	trace[c]
10	$4\text{-}FC_6H_4COCl$	1	79
11	$4\text{-}NO_2C_6H_4COCl$	0.5	75
12	$4\text{-}ClC_6H_4CH{=}CHCOCl$	4	60
13	$CH_2{=}CHCOCl$	4	70
14	$4\text{-}MeC_6H_4OTf$	20	90
15		20	90
16	$C_6H_5CH{=}CHCH_2Cl$	20	80
17	$CH_2{=}CHCH_2Br$	20	70[d]
18	$CH_2{=}CCH_3Br$	20	50[d]

[a] All reactions were carried on 1 mmol scale with 1.2 mmol of **1** in the presence of 2 mol % catalyst. [b] All are isolated yields and are not optimized. [c] Bisindole was the major product. [d] Excess of the allyl bromide (entry 16) and bromopropene (entry 17) were used; the yield was calculated based on the stannane.

of the desired sulfones. In this case bisindole was the major product. Similar exclusive formation of the homocoupling product has been observed in the palladium-catalyzed coupling reaction between (phenylethynyl)-tributylstannane and arylsulfonyl chlorides.[9] The coupling of **1** with 5-iodouracil afforded only moderate yield of the desired coupling product (entry 7, Table 1).

N-Protected Indol-2-ylstannanes. In order to expand the utility of this synthetic methodology, we sought to examine the coupling of N-protected indol-2-ylstannanes. The N-*tert*-butoxycarbonyl protecting group was chosen because of the ease of protection and deprotection.[3e,10] Lithiation of *N*-(*tert*-butoxycarbonyl)indole at −78 °C with *n*-butyllithium and subsequent trapping of the resulting 2-lithio species with tributyltin chloride provided [*N*-(*tert*-butoxycarbonyl)indol-2-yl]tributylstannane (**3**) in 40% yield after chromatographic purification. The coupling of 4-methoxybenzyl bromide with the stannane **3**, under the same conditions as for **1** did not afford expected product. However, the coupling reaction proceeded smoothly at higher temperature (refluxing dioxane) to provide the coupled product (entries 1−8, Table 2). The presence of an electron-withdrawing substituent on the nitrogen substantially decreases the reactivity of the stannane **3** as evidenced by the decreased reactivity of such indoles toward electrophiles.[11] In general, lower yields were obtained with **3** compared to **1**, and the reaction was very sluggish with allyl and vinyl bromides. Vinyl and aryl triflates failed to provide the desired products and destannylation occurred exclusively to

Table 2. Coupling Reactions of N-Protected Indol-2-yltributylstannanes[a]

entry	prot. group	RX	% yield of A[b]	% yield of B[b,c]
1	BOC	$MeOC_6H_4CH_2Br$	50	85
2		3-bromopyridine	66[d]	92
3		$4\text{-}CHOC_6H_4Br$	62	*e*
4		$4\text{-}CNC_6H_4Br$	66	86
5		$4\text{-}EtOOCC_6H_4I$	68	85
6		$C_6H_5CH{=}CHCH_2Cl$	72	72
7		$4\text{-}FC_6H_4COCl$	59	95
8		$4\text{-}MeC_6H_4OTf$	–	
9	SEM	$4\text{-}EtOOCC_6H_4I$	90	56[f]
10		$4\text{-}CNC_6H_4Br$	94	60
11			60	*g*
12		$4\text{-}MeC_6H_4OTf$	66	60
13			61	57
14		$CH_2{=}CHCH_2Br$	62	72[h]
15		$CH_2{=}CCH_3Br$	50	82

[a] All reactions were carried on 1 mmol scale with 1.2 mmol of **3** or **4** in the presence of 2 mol % catalyst. [b] All are isolated yields and are not optimized. [c] Yield of the deprotection step. [d] Required 4 mol % the catalyst. [e] Deprotection occurred smoothly but the product was unstable. [f] Mixture of ethyl ester and the acid. [g] Only a trace of deprotection occurred. [h] Deprotection occurred with the formation of 2-propenylindole (*E*:*Z* = 80:20).

generate the *N*-(*tert*-butoxycarbonyl)indole. Only a trace amount of the desired product was observed with 5-iodouracil. Removal of the *tert*-butoxycarbonyl group was achieved using trifluoroacetic acid in excellent yield. Although deprotection went smoothly in case of *N*-(*tert*-butoxycarbonyl)-2-(4-formylphenyl)indole, the deprotected product, 2-(4-formylphenyl)indole, was unstable (entry 3, Table 2).

Although the *tert*-butoxycarbonyl is an adequate protecting group, its electron-withdrawing nature limits the utility of the stannane **3** in the synthesis of the 2-substituted indoles. In order to eliminate such limitations, the [(trimethylsilyl)ethoxy]methyl protecting group, which does not alter the reactivity of the indole nucleus and yet can be removed under facile conditions, was examined.[3cd,12] Metalation of *N*-[[(trimethylsilyl)ethoxy]-methyl]indole was best performed with *tert*-butyllithium in a 3:2 mixture of hexane/ether between 0 to 20 °C.[3c,d, 12] The stannane **4** is unstable on silica gel, like that of **1**, but could be purified by distillation. As expected, the coupling of *N*-[[(trimethylsilyl)ethoxy]methyl]indol-2-ylstannane (**4**) proceeded smoothly in THF at reflux (entries 9−15, Table 2). Unlike reagent **3**, stannane **4** reacted with triflates, allyl and vinyl bromides, as well as 5-iodouracil. The removal of the [(trimethylsilyl)-ethoxy]methyl group, however, initially proved difficult. The reported literature procedure, using tetra-*n*-butylammonium fluoride/THF to remove the [(trimethylsilyl)-ethoxy]methyl group of the protected indoles and pyrroles gave poor yield.[3c,d] This observation is similar to that observed by the other authors.[12] The best and consistent results were obtained by tetra-*n*-butylammonium fluoride in DMF in the presence of an excess of ethylenediamine.[12,13] Partial saponification of the ethyl ester oc-

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curred under the reaction conditions (entry 9, Table 2). In the case of 2-(uracil-5-yl)indole, only a trace amount of the deprotection occurred (entry 11, Table 2). The removal of the [(trimethylsilyl)ethoxy]methyl group occurred with the rearrangement of the allyl group, thus forming 2-propenylindole (80/20 mixture of *E*/*Z*) as the final product (entry 14, Table 2) in the case of *N*-[[(trimethylsilyl)ethoxy]methyl]-2-allylindole.

In summary, indol-2-ylstannanes behave very similarly to the arylstannanes. *N*-Alkylindol-2-ylstannanes are very reactive, but the *N*-*tert*-butoxycarbonyl group decreases the activity toward coupling. *N*-Methyl- and *N*-[[(trimethylsilyl)ethoxy]methyl]stannylindoles react with a variety of coupling partners with high yields under mild conditions. In the case of *N*-(*tert*-butoxycarbonyl)stannylindole, however, a few restrictions are encountered thus limiting the scope. Such limitations in the coupling reactions are eliminated by selecting the [(trimethylsilyl)-ethoxy]methyl protecting group, and the removal of the [(trimethylsilyl)ethoxy]methyl group can be achieved with reasonable ease. In this paper, we have shown that the indol-2-ylstannanes provide a precursor for convergent synthesis of a variety of 2-substituted indoles. The groups such as cyano, ester, formyl, and nitro, which are sensitive to the reaction conditions used in the alternate methods (e.g. lithium species, hydrazines in the Fischer indole synthesis) are tolerated in this methodology. Thus, this methodology provides an excellent alternative to the existing technology for 2-substituted indoles.[3,5,14]

Experimental Section

^{1}H NMR spectra were obtained on a Bruker ACF-300 spectrometer. Chemical shifts are reported in parts per million (δ scale) relative to tetramethylsilane as internal standard. IR spectra were recorded on a Pye-Unicam 3-200 spectrometer. Melting points were recorded on Mettler-FP90 with FP81 cell and are uncorrected. Flash chromatography was performed on 230–400 mesh silica gel.

(*N*-Methylindol-2-yl)tributylstannane (1). To a solution of *N*-methylindole (20 g, 0.15 mol) in dry THF (200 mL) at 0 °C under N_2 was added *n*-butyllithium (61.0 mL, 2.5 M, 0.15 mol) dropwise with stirring so as to keep the temperature below 5 °C. After the addition was complete the heterogeneous mixture was allowed to react for 2 h between 0–5 °C. The reaction mixture was then cooled in a dry ice–acetone bath and tributyltin chloride (48.7 g, 0.15 mol) was added. The reaction mixture allowed to warm to room temperature, diluted with ethyl acetate and washed with water and brine, dried (sodium sulfate), and concentrated. The pure product was obtained by distillation (50 g, 78%): bp 145–155 °C (0.05 mmHg); NMR ($CDCl_3$) δ 7.60 (bd, J = 7.8 Hz, 1 H), 7.31 (bd, J = 8.2 Hz, 1 H), 7.15 (ddd, J = 8.2, 8.2, 1.1 Hz, 1 H), 7.07 (ddd, J = 8.2, 7.8, 0.9 Hz, 1 H), 6.60 (s, 1 H), 3.80 (s, 3 H), 1.6–0.9 (m, 27 H); mass spectrum m/e 421 (M^+).

General Procedure for the Coupling of 1. *N*-Methyl-2-benzylindole. The coupling **1** with benzyl chloride is representative: A mixture of benzyl chloride (0.125 g, 1.0 mmol), the stannane **1** (0.520 g, 1.2 mmol), and the catalyst **2** (0.015 g, 0.02 mmol) in dry THF (5 mL) was heated at reflux temperature for 1 h under N_2. The reaction mixture was cooled, diluted with ethyl acetate, and stirred over 15% potassium fluoride solution (20 mL) for 15 min. The precipitate was removed by filtration and was washed well with ethyl acetate. The ethyl acetate layer was separated, washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by flash chromatography (hexane) to give *N*-methyl-2-benzylindole: mp 60.6–61.3 °C (hexane) [lit.[15] 65 °C]. Anal. Calcd for $C_{16}H_{15}N$ (MW 221.30): C, 86.83; H, 6.84; N, 6.33. Found: C, 86.69; H, 6.68; N, 6.14.

In a similar manner the following compounds were obtained.

***N*-Methyl-2-[(4-nitrophenyl)methyl]indole**: mp 135.5–136.3 °C (hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 2 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.33 (d, J = 8.8 Hz, 2 H), 7.27 (d, J = 8.8 Hz, 1 H), 7.20 (ddd, J = 1.0, 7.0, 8.8 Hz, 1 H), 7.15 (ddd, J = 1.0, 8.0, 7.0 Hz, 1 H), 6.3 (s, 1 H), 4.25 (s, 2 H), 3.55 (s, 3 H). Anal. Calcd for $C_{16}H_{14}N_2O_2$ (MW 266.30): C, 72.15; H, 5.30; N, 10.53. Found: C, 71.77; H, 5.24; N, 10.36.

***N*-Methyl-2-(3-pyridyl)indole:** mp 85.2–86.1 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$) δ 8.82 (d, J = 2.3 Hz, 1 H), 8.68 (dd, J = 2.3, 4.9 Hz, 1 H), 7.85 (dm, J = 7.9 Hz, 1 H), 7.69 (d, J = 8.0 Hz, 1 H), 7.46–7.32 (dd and d, J = 5.5, 4.4 and 8.5 Hz, 4 H), 7.28 (ddd, J = 1.1, 7.2, 7.5 Hz, 1 H), 7.17 (ddd, J = 1.0, 8.2, 7.2 Hz, 1 H), 6.66 (s, 1 H), 3.78 (s, 3 H). Anal. Calcd for $C_{14}H_{12}N_2$·0.25H_2O (MW 212.77): C, 79.03; H, 5.92; N, 13.16. Found: C, 79.21; H, 5.64; N, 13.23.

***N*-Methyl-2-toluylindole**: mp 92.5–93.1 °C (hexane, lit.[2c,16] 94–95 °C). Anal. Calcd for $C_{16}H_{15}N$ (MW 221.30): C, 86.83; H, 6.84; N, 6.33. Found: C, 87.03; H, 6.94; N, 6.32.

***N*-Methyl-2-(4-cyanophenyl)indole**: mp 163.1–163.6 °C (hexane/ethyl acetate); IR (KBr) 2224 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 8.5 Hz, 2 H), 7.63 (dd, J = 0.8, 7.8 Hz, 1 H), 7.58 (d, J = 8.6 Hz, 2 H), 7.36 (dd, J = 0.9, 7.4 Hz, 1 H), 7.28 (ddd, J = 1.1, 8.6, 6.9 Hz, 1 H), 7.16 (ddd, J = 1.1, 7.8, 6.9 Hz, 1 H), 6.64 (d, J = 0.6 Hz, 1 H), 3.74 (s, 3 H). Anal. Calcd for $C_{15}H_{12}N_2$ (MW 220.28): C, 82.73; H, 5.20; N, 12.06. Found: C, 82.52; H, 5.27; N, 11.83.

***N*-Methyl-2-[4-(ethoxycarbonyl)phenyl]indole:** mp 103.8–104.7 °C (ethyl acetate/hexane); IR (KBr) 1711 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.0 Hz, 1 H), 7.61 (d, J = 8.3 Hz, 2 H), 7.40 (d, J = 8.5 Hz, 1 H), 7.28 (ddd, J = 1.1, 8.5, 7.5 Hz, 1 H), 7.18 (ddd, J = 1.0, 8.0, 7.5 Hz, 1 H), 6.67 (s, 1 H), 4.45 (q, 2 H), 3.80 (s, 3 H), 1.45 (t, 3 H). Anal. Calcd for $C_{18}H_{17}NO_2$ (MW 279.34): C, 77.38; H, 6.14; N, 5.02. Found: C, 77.53; H, 6.39; N, 4.96.

***N*-Methyl-2-(uracil-5-yl)indole:** mp >280 °C; IR (KBr) 1755, 1716, 1682 cm^{-1}; ^{1}H NMR (d_6-DMSO) δ 11.34 (bs, 1 H), 7.59 (s, 1 H), 7.50 (d, J = 7.7 Hz, 1 H), 7.41 (d, J = 8.3 Hz, 1 H), 7.15 (dd, J = 8.3, 7.0 Hz, 1 H), 7.05 (dd, J = 7.7, 7.0 Hz, 1 H), 3.58 (s, 3 H). Anal. Calcd for $C_{13}H_{11}N_3O_2$ (MW 241.25): C, 64.72; H, 4.59; N, 17.15. Found: C, 64.55; N, 4.55; N, 17.15.

***N*-Methyl-2-(2-formylthien-4-yl)indole:** mp 158.3–159.1 °C (hexane/ethyl acetate); IR (KBr) 1666 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 9.97 (d, J = 1.2 Hz, 1 H), 7.90 (d, J = 1.4 Hz, 1 H), 7.76 (m, 1 H), 7.63 (d, J = 7.9 Hz, 1 H), 7.35 (d, J = 8.2 Hz, 1 H), 7.28 (ddd, J = 1.2, 8.2, 7.0 Hz, 1 H), 7.15 (ddd, J = 1.1, 7.9, 7.0 Hz, 1 H), 6.62 (s, 1 H), 3.79 (s, 3 H). Anal. Calcd for $C_{14}H_{11}NOS$ (MW 241.31): C, 69.68; H, 4.59; N, 5.8. Found: C, 70.03; H, 4.65; N, 5.82.

***N*-Methyl-2-(4-fluorobenzoyl)indole**: mp 82.0–83.3 °C (hexane); IR (KBr) 1635 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 7.99–7.95 (m, 2 H), 7.70 (md, J = 8.2 Hz, 1 H), 7.49–7.41 (m, 2 H), 7.21–7.18 (m, 3 H), 7.01 (s, 1 H), 4.13 (s, 3 H). Anal. Calcd for $C_{16}H_{12}FNO$ (MW 253.28): C, 75.86; H, 4.78; N, 5.53. Found: C, 75.48; H, 4.72; N, 5.37.

***N*-Methyl-2-(4-nitrobenzoyl)indole:** mp 141.2–141.8 °C (ethyl acetate/hexane); IR (KBr) 1643 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 8.38 (d, J = 8.8 Hz, 2 H), 8.05 (d, J = 8.7 Hz, 2 H), 7.70 (d, J = 8.2 Hz, 1 H), 7.48 (m, 2 H), 7.23–7.19 (m, 1 H), 7.01 (s, 1 H), 4.18 (s, 3 H). Anal. Calcd for $C_{16}H_{12}N_2O_3$ (MW 280.28): C, 68.56; H, 4.31; N, 9.99. Found: C, 68.32; H, 4.23; N, 9.77.

***N*-Methyl-2-(4-chlorocinnamoyl)indole:** mp 192.9–193.5 °C (hexane/ethyl acetate); IR (KBr) 1651 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 7.78–7.70 (m, 2 H), 7.60–7.50 (m, 3 H), 7.42–7.37 (m, 5H), 7.20–7.15 (m, 1 H), 4.15 (s, 3 H). Anal. Calcd for $C_{18}H_{14}ClNO$ (MW 295.77): C, 73.09; H, 4.77; N, 4.73. Found: C, 73.01; H, 4.84; N, 4.62.

***N*-Methyl-2-acryloylindole:** mp 42.7–45.0 °C; IR (KBr) 1655 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1 H), 7.40 (dd, J = 4.6, 1.1 Hz, 2 H), 7.32 (s, 1 H), 7.24–7.13 (m, 2

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H), 6.48 (dd, J = 20, 1.8 Hz, 1 H), 5.83 (dd, J = 10.4, 1.8 Hz, 1 H), 4.10 (s, 3 H). Anal. Calcd for $C_{12}H_{11}NO$ (MW 185.23): C, 77.81; H, 5.98; N, 7.56. Found: C, 78.13; H, 6.04; N, 7.85.

***N*-Methyl-2-(4-phenylcyclohexen-1-yl)indole:** mp 150–151 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$) δ 7.57 (bd, 1 H), 7.37–7.17 (m, 7 H), 7.09 (dd, J = 8.0, 7.1 Hz, 1 H), 6.4 (s, 1 H), 6.01 (m, 1 H), 3.75 (s, 3 H), 3.0–2.9 (m, 1 H), 2.6–2.3 (m, 3 H), 2.18–1.9 (m, 3 H). Anal. Calcd for C_{21} $H_{21}N$ (MW 287.40): C, 87.76; H, 7.36; N, 4.87. Found: C, 87.65; H, 7.26; N, 4.84.

***N*-Methyl-2-cinnamylindole:** mp 67.6–70.9 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 1 H), 7.40–7.08 (m, 8 H), 6.48–6.29 (m, 3 H), 3.72–3.65 (m, 5 H). Anal. Calcd for C_{18} $H_{17}N$ (MW 247.34): C, 87.39, H; 6.93; N, 5.67. Found: C, 87.61; H, 6.92; N, 6.03.

***N*-Methyl-2-allylindole:** oil, ^{1}H NMR ($CDCl_3$) δ 7.52 (bd, J = 7.7 Hz, 1 H), 7.25 (d, J = 8.1 Hz, 1 H), 7.16 (ddd, J = 1.4, 7.1, 8.1 Hz, 1 H), 7.09 (ddd, J = 1.1, 7.1, 7.7 Hz, 1 H), 6.28 (s, 1 H), 6.07–5.94 (m, 1 H), 5.17–5.09 (m, 2 H), 3.64 (s, 3 H), 3.52 (bd, J = 6.3 Hz, 2 H); mass spectrum m/e 171 (M^+).

***N*-Methyl-2-(2-propenyl)indole:** oil, ^{1}H NMR ($CDCl_3$) δ 7.57 (bd, J = 7.8 Hz, 1 H), 7.29 (d, J = 8.2 Hz, 1 H), 7.21 (ddd, J = 1.1, 7.0, 8.2 Hz, 1 H), 7.11 (ddd, J = 1.0, 7.8, 7.0 Hz, 1 H), 6.46 (s, 1 H), 5.36–5.34 (m, 1 H), 5.16 (bs, 1 H), 3.76 (s, 3 H), 2.18 (d, J = 1.1 Hz, 3 H). Anal. Calcd for C_{12} $H_{13}N$ (MW 171.24): C, 84.16; H, 7.65; N, 8.18. Found: C, 84.58; H, 7.58; N, 8.41.

[*N*-(*tert*-Butoxycarbonyl)indol-2-yl]tributylstannane (3). To a stirred solution of *N*-(*tert*-butoxycarbonyl)indole (11.6 g, 53 mmol) in dry THF (150 mL) at −78 °C was added butyllithium (33 mL, 1.6 M, 53 mmol) dropwise. The resulting yellow solution was allowed to react for 2 h at −78 °C and then tributyltin chloride (17.2 g, 53 mmol) in dry THF (50 mL) was added dropwise. The reaction mixture was stirred for 0.5 h and allowed to warm to −20 °C when it was quenched with water. The reaction mixture was diluted with ethyl acetate, washed with water followed by brine, and then dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (silica gel, hexane) to obtain **3** (11.0 g, 40%): ^{1}H NMR ($CDCl_3$) δ 7.97 (bd, J = 8.0 Hz, 1 H), 7.54 (d, J = 6.9 Hz), 7.28–7.18 (m, 2 H), 6.74 (s, 1 H), 1.73 (s, 9 H), 1.6–0.8 (m, 27 H); mass spectrum m/e 394 [M^+ − (t-Bu-n-Bu) + 1].

General Method for the Coupling of 3. The coupling reactions were performed in a similar manner to the coupling with the stannane **1** except that the reactions were carried out in dioxane at 100 °C overnight. The reactions were worked up as described for *N*-methylstannane.

1-(*tert*-Butoxycarbonyl)-2-(4-methoxybenzyl)indole: mp 95.1–96.5 °C; IR (KBr) 1724 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 1 H), 7.38 (dd, J = 1.1, 7.7 Hz, 1 H), 7.2 (dd, J = 1.1, 8.4 Hz, 1 H), 7.15 (dd, J = 1.2, 7.8 Hz, 1 H), 7.13 (d, J = 8.8 Hz, 2 H), 6.86 (d, J = 8.7, 2 H), 6.08 (bs, 1 H), 4.29 (s, 2 H), 3.80 (s, 3 H), 1.59 (s, 9 H). Anal. Calcd for $C_{21}H_{23}NO_3 \cdot 0.4H_2O$ (MW 344.6): C, 73.18; H, 6.87; N, 4.15. Found: C, 73.31; H, 6.82; N, 4.10.

***N*-(*tert*-Butoxycarbonyl)-2-(3-pyridyl)indole**: mp 69–71.9 °C; IR (KBr) 1728 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 8.69 (d, J = 2.1 Hz, 1 H), 8.60 (dd, J = 4.8, 1.6 Hz, 1 H), 8.23 (bd, J = 8.3 Hz, 1 H), 7.72 (s, 1 H), 7.59 (bd, J = 8.3 Hz, 1 H), 7.4–7.3 (m, 2 H), 7.27 (ddd, J = 1.1, 7.4, 8.3 Hz, 1 H), 1.35 (s, 9 H). Anal. Calcd for $C_{18}H_{18}N_2O_2$ (MW 294.35): C, 73.44; H, 6.16; N, 9.51. Found: C, 73.12; H, 6.16; N, 9.28.

***N*-(*tert*-Butoxycarbonyl)-2-(4-formylphenyl)indole:** mp 118.9–120.1 °C; IR (KBr) 1732 (CO), 1699 (CHO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.06 (s, 1 H), 8.20 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 2 H), 7.60 (m, 2 H), 7.37 (ddd, J = 1.5, 8.6, 8.3 Hz, 1 H), 7.27 (ddd, J = 1.0, 7.6, 8.0 Hz, 1 H), 6.66 (s, 1 H), 1.34 (s, 9 H). Anal. Calcd for $C_{20}H_{19}NO_3$ (MW 321.38): C, 74.75; H, 6.14; N, 4.56. Found: C, 74.72; H, 6.14; N, 4.56.

***N*-(*tert*-Butoxycarbonyl)-2-(4-cyanophenyl)indole**: mp 121.8–122.9 °C; IR (KBr) 2229 (CN), 1728 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.2 (d, J = 8.2 Hz, 1 H), 7.7 (d, J = 8.2 Hz, 2 H), 7.57 (d, J = 7.6 Hz, 1 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.37 (ddd, J = 1.2, 7.2, 8.2 Hz, 1 H), 7.28 (ddd, J = 1.0, 7.6, 7.2 Hz, 1 H), 6.66 (s, 1 H), 1.37 (s, 9 H). Anal. Calcd for $C_{20}H_{18}N_2O_2$ (MW 318.38): C, 75.96; H, 5.67; N, 8.80. Found: C, 75.78; H, 5.47; N, 8.58.

***N*-(*tert*-Butoxycarbonyl)-2-(4-carbethoxyphenyl)indole**: mp 102.9–103.1 °C (hexane); IR (KBr) 1736, 1713 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.2 (dd, J = 0.8, 8.3 Hz, 1 H), 8.08 (d, J = 8.5 Hz, 2 H), 7.57 (dd, J = 1.1, 8.2 Hz, 1 H), 7.49 (d, J = 8.6 Hz, 2 H), 7.35 (ddd, J = 1.4, 8.2, 7.4 Hz, 1 H), 7.26 (ddd, J = 1.1, 8.3, 7.4 Hz, 1 H), 6.62 (d, J = 0.7 Hz, 1 H), 4.41 (q, 2 H), 1.42 (t, 3 H), 1.33 (s, 9 H). Anal. Calcd for $C_{22}H_{23}NO_4 \cdot 0.15H_2O$ (MW 368.13): C, 71.77; N, 6.37; N, 3.80. Found: 71.84; H, 6.35; N, 3.76. Mass spectrum m/e 365 (M^+).

***N*-(Butoxycarbonyl)-2-cinnamylindole**: oil; IR (film) 1732 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 1 H), 7.45 (dd, J = 7.3, 1.5 Hz, 1 H), 7.4- 7.15 (m, 7 H), 6.52–6.39 (m, 3 H), 3.91 (brd, J = 4.1 Hz, 2 H), 1.67 (s, 9 H). Anal. Calcd for C_{23} $H_{23}NO_2$ (MW 345.44): C, 79.97; H, 6.71; N, 4.05. Found: C, 79.62; H, 6.58; N, 4.19.

***N*-(Butoxycarbonyl)-2-(4-fluorobenzoyl)indole:** mp 71.7–72.2 °C; IR (KBr) 1740, 1666 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.20 (d, J = 8.2 Hz, 2 H), 7.98–7.93 (m, 2 H), 7.63 (d, J = 7.8 Hz, 1 H), 7.45 (ddd, J = 1.1, 7.8, 7.0, Hz, 1 H), 7.30 (ddd, J = 1.2, 8.2, 7.0, 1.0 Hz, 1 H), 7.15 (dd, J = 8.5, 8.6 Hz, 2 H), 6.91 (s, 1 H), 1.39 (s, 9 H). Anal. Calcd for $C_{20}H_{18}FNO_3$ (MW 339.3): C, 70.78; H, 5.34; N, 4.12. Found: C, 70.90; H, 5.51; 4.37.

General Method for the Deprotection of *tert*-Butoxycarbonyl Group. A mixture of the substrate (0.5 mmol), trifluoroacetic acid (2 mL), and dichloromethane (2 mL) was stirred at room temperature for 0.5–2 h. The resulting mixture was concentrated and the residue was purified by flash chromatography. The following compounds were obtained in this manner from the corresponding N-protected derivatives.

2-(4-Methoxybenzyl)indole: mp 109.0–111.4 °C (hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 7.52 (dd, J = 0.8, 7.8 Hz, 1 H), 7.24 (d, J = 7.9 Hz, 1 H), 7.15 (d, J = 8.7 Hz, 2 H), 7.13–7.03 (m, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 6.3 (m, 1 H), 4.06 (s, 2 H), 3.80 (s, 3 H). Anal. Calcd for $C_{16}H_{15}NO$ (MW 237.3): C, 80.98; H, 6.37; N, 5.90. Found: C, 80.89; H, 6.28; N, 6.15.

2-(3-Pyridyl)indole: mp 175.8–176.9 °C (hexane/ethyl acetate) [lit.[17] 173–175 °C (ethanol/water)].

2-(4-Cyanophenyl)indole: mp 198–198.4 °C (hexane/ethyl acetate) [lit.[18] 194–195 °C (methanol)].

2-[4-(Carbethoxy)phenyl]indole: mp 216.9–217.8 °C; IR (KBr) 1693 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 8.09 (d, J = 8.5 Hz, 2 H), 7.77 (d, J = 8.5 Hz, 2 H), 7.63 (d, J = 7.4 Hz, 1 H), 7.42 (d, J = 8.2 Hz, 1 H), 7.20 (ddd, J = 1.2, 7.0, 8.2 Hz, 1 H), 7.13 (ddd, J = 1.1, 7.4, 7.0 Hz, 1 H), 6.94 (d, J = 1.5 Hz, 1 H), 4.4 (q, 2 H), 1.4 (t, 3 H). Anal. Calcd for $C_{17}H_{15}NO_2$ 0.3 H_2O (MW 2270.72): C, 75.42; H, 5.80; N, 5.17. Found: C, 75.21; H, 5.83; N, 5.05.

2-Cinnamylindole: mp 90.3–91.8 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.95 (bs, 1 H), 7.54 (dd, J = 1.4, 7.6 Hz, 1 H), 7.42–7.22 (m, 7 H), 7.18–7.04 (m, 2 H), 6.57 (d, J = 15.8 Hz, 1 H), 6.42–6.33 (m, 2 H), 3.70 (d, J = 6.7 Hz, 2 H). Anal. Calcd for $C_{17}H_{15}N$ (MW 233.3): C, 87.51; H, 6.48; N, 6.00. Found: C, 87.43; H, 6.49; N, 6.15.

2-(4-Fluorobenzoyl)indole: mp 185.2–185.6 °C (hexane/ethyl acetate); IR (KBr) 1626 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 9.33 (bs, 1 H), 8.06–8.01 (m, 2 H), 7.73 (d, J = 7.4 Hz, 1 H), 7.49 (d, J = 9.1 Hz, 1 H), 7.39 (ddd, J = 1.0, 7.0, 9.1 Hz, 1 H), 7.25- 7.18 (m, 3 H), 7.15–7.14 (m, 1 H). Anal. Calcd for $C_{15}H_{10}FNO$ (MW 239.25): C, 75.30; H, 4.21; N, 5.85. Found: C, 75.20; H, 3.98; N, 6.17.

Preparation of *N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(tributylstannyl)indole (4). To a solution of *N*-[[(trimethylsilyl)oxy]methyl]indole (9.5 g, 34 mmol) in a mixture of ether/hexane (40:60 mL) between 0 and 10 °C was added *tert*-butyllithium (24.3 mL, 1.4 M, 34 mmol), and the reaction mixture was allowed to warm to room temperature. The reaction was stirred at room temperature for 1 hour and then cooled to −78 °C, tributyltin chloride (11.0 g, 34 mmol) in ether

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was added dropwise, and the reaction was allowed to warm to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was washed with water followed by brine, dried (Na_2SO_4), and concentrated, and the residue was distilled under reduced pressure: bp 124–130 °C (0.04 mmHg, 13 g, 77%): ^{1}H NMR ($CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1 H), 7.49 (d, J = 8.1 Hz, 1 H), 7.2–7.15 (m, 1 H), 7.1 (ddd, J = 1.1, 7.5, 6.9 Hz, 1 H), 6.33 (dd, J = 0.8, 13.3 Hz, 1 H), 5.47 (s, 2 H), 3.45 (dd, J = 7.2, 7.1 Hz, 2 H), 1.62–0.9 (m, 29 H), −0.03 (s, 9 H); mass spectrum m/e 480 (M^+ − Bu).

General Procedure for the Coupling of 4. The coupling was carried out in a similar manner to the coupling with **1** (Table 2).

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(4-carbethoxyphenyl)indole:** oil; IR (KBr) 1716 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.65 (d, J = 7.5 Hz, 1 H), 7.52 (d, J = 8.2 Hz, 1 H), 7.30 (ddd, J = 1.2, 8.2, 7.1 Hz, 1 H), 7.20 (ddd, J = 0.9, 7.5, 7.1 Hz, 1 H), 6.67 (s, 1 H), 5.46 (s, 2 H), 4.41 (q, 2 H), 3.56 (dd, J = 8.1, 8.3, 2 H), 1.40 (t, 3 H), 0.93 (dd, J = 8.3, 8.1, 2 H), −0.03 (s, 9 H). Anal. Calcd for $C_{23}H_{29}NO_3Si$ (MW 395.58): C, 69.83; H, 7.38; N, 3.54. Found: C, 68.48; H, 7.34; N, 3.47; mass spectrum m/e 395 (M^+).

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(4-cyanophenyl)indole:** oil; IR (neat) 2226 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2 H), 7.75 (d, J = 8.6 Hz, 2 H), 7.65 (d, J = 7.7 Hz, 1 H), 7.52 (d, J = 8.2 Hz, 1 H), 7.32 (ddd, J = 1.2, 7.1, 8.2 Hz, 1 H), 7.20 (ddd, J = 1.0, 7.1, 7.7 Hz, 1 H), 6.73 (s, 1 H), 5.44 (s, 2 H), 3.62 (dd, J = 8.1, 8.2, 2 H), 0.93 (dd, J = 8.2, 8.1 Hz, 2 H), −0.02 (s, 9 H). Anal. Calcd for $C_{21}H_{24}N_2OSi$ (348.53): C, 72.37; H, 6.94; N, 8.03. Found: C, 72.09; H, 6.97; N, 8.07.

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(uracil-5-yl)indole:** mp 194.9–195.6 °C; IR (KBr); ^{1}H NMR ($CDCl_3$) δ 9.91 (bs, 1 H,), 9.77 (bs, 1 H,), 7.61 (d, J = 5.8 Hz, 1 H), 7.56 (d, J = 7.8 Hz, 1 H), 7.43 (d, J = 8.3 Hz, 1 H), 7.24 (dd, J = 7.1, 8.3 Hz, 1 H), 7.13 (dd, J = 7.1, 7.8 Hz, 1 H), 6.62 (s, 1 H), 5.47 (s, 2 H), 3.38 (dd, J = 8.3, 8.4 Hz, 2 H); 0.85 (d, J = 8.4, 8.3 Hz, 2 H), −0.09 (s, 9 H). Anal. Calcd for $C_{18}H_{23}N_3O_3Si$ (MW 357.49): C, 60.47; H, 6.48; N, 11.75. Found: C, 60.78; H, 6.41; N, 11.64.

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(4-toluyl)indole:** oil; ^{1}H NMR ($CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1 H), 7.55–7.51 (m, 3 H), 7.31–7.23 (m, 3 H), 7.18 (ddd, J = 0.8, 7.0, 7.5 Hz, 1 H), 6.58 (d, J = 0.7 Hz, 1 H), 5.48 (s, 2 H), 3.52 (2 H), 2.43 (s, 3 H), 0.88 (2 H), -0.03 (s, 9 H). Anal. Calcd for $C_{21}H_{27}NOSi$ (MW 337.54): C, 74.72, H, 8.06; N, 4.14. Found: C, 74.73; H, 8.21; N, 4.41.

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(4-phenylcyclohexen-1-yl)indole:** oil; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1 H), 7.46 (d, J = 7.45 Hz, 1 H), 7.40–7.19 (m, 6H), 7.10 (ddd, J = 1.1, 7.5, 7.0 Hz, 1 H), 6.44 (s, 1 H), 6.24 (m, 1 H), 5.47 (s, 2 H), 3.55 (dd, J = 8.08, 8.23 Hz, 2 H), 3.0–2.85 (m, 1 H), 2.65–2.30 (m, 3 H), 2.2–1.9 (m, 2 H), 0.94 (dd, J = 8.23, 8.08 Hz, 2 H), −0.02 (s, 9 H); mass spectrum m/e 403 (M^+).

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-allylindole:** oil; ^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 7.3 Hz, 1 H), 7.45 (d, J = 8.1 Hz, 1 H), 7.23 (ddd, J = 1.4, 7.3, 8.1 Hz, 1 H), 7.16 (ddd, J = 1.2, 7.8, 7.3 Hz, 1 H), 6.38 (brs, 1 H), 6.16–6.0 (m, 1 H), 5.51 (s, 2 H), 5.21–5.29 (m, 2 H), 3.6 (md, J = 7.3 Hz, 2 H), 3.5 (dd, J = 8.0, 8.1 Hz, 2 H), 0.91 (dd, J = 8.1, 8.0 Hz, 2 H), −0.05 (s, 9 H). Anal. Calcd for $C_{17}H_{25}NOSi$ (287.48): C, 71.02; H, 8.76; N, 4.87. Found: C, 70.60; H, 8.72; N, 4.82. Mass spectrum m/e 287 (M^+).

***N*-[[(Trimethylsilyl)ethoxy]methyl]-2-(propen-2-yl)indole:** oil; ^{1}H NMR ($CDCl_3$) δ 7.60 (dd, J = 1.0, 7.8 Hz, 1 H), 7.46 (dd, J = 1.1, 8.1 Hz, 1 H), 7.24 (ddd, J = 1.1, 8.1, 7.1 Hz, 1 H), 7.13 (ddd, J = 1.1, 7.1, 7.8 Hz, 1 H), 6.51 (d, J = 0.7 Hz, 1 H), 5.49 (s, 2 H), 5.44 (bs, 1 H), 5.37 (m, 1 H), 3.59 (dd, J = 7.3, 7.2 Hz, 2 H), 2.2 (dd, J = 0.8, 1.0 Hz, 3 H), 0.93 (dd, J = 7.1, 7.4 Hz, 2 H), −0.02 (s, 9 H); mass spectrum m/e 287 (M^+).

Procedure for the Removal of the [(Trimethylsilyl)ethoxy]methyl Group. A mixture of the substrate (0.5 mmol), tributylammonium fluoride (1.5 mL of 1 M solution in THF) was concentrated on a rotary evaporator. The residue was dissolved in DMF (1 mL) and ethylenediamine (0.15 mL), and the mixture was heated at 80 °C for 20 h. The resulting greenish mixture was diluted with ethyl acetate and washed with dilute hydrochloric acid followed by brine and dried (Na_2SO_4). The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography. The following compounds were thus obtained.

2-(4-Carboxyphenyl)indole: mp >280 °C; IR (KBr) 1682 (CO) cm^{-1}; ^{1}H NMR (d_6-DMSO) δ 12.89 (bs, 1 H), 11.68 (bs, 1 H), 8.0 (m, 4H), 7.56 (d, J = 7.9 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 1 H), 7.16 (ddd, J = 1.1, 8.1, 8.2 Hz, 1 H), 7.04 (s, 1 H), 7.01 (dd, J = 8.1, 6.9 Hz, 1 H), mass spectrum m/e 237 (M^+).

2-(4-Toluyl)indole: mp 219.2–220.3 °C (lit.[19] 220.5–221 °C).

2-(4-Phenylcyclohexen-1-yl)indole: mp 205.3–205.6 °C; ^{1}H NMR ($CDCl_3$) δ 8.13 (bs, 1 H), 7.56 (d, J = 7.7 Hz, 1 H), 7.38–7.20 (m, 6H), 7.15 (ddd, J = 1.2, 7.1, 7.8 Hz, 1 H), 7.07 (ddd, J = 1.1, 7.7, 7.1 Hz, 1 H), 6.48 (d, J = 1.0 Hz, 1 H), 6.2 (m, 1 H), 2.8–1.85 (m, 7H). Anal. Calcd for $C_{20}H_{19}N$ (273.38): C, 87.87; H, 7.00; N, 5.12. Found: C, 87.89; H, 6.84; N, 5.36.

2-[(*E*)-Propen-1-yl)]indole: mp 94.8–95.5 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 7.96 (bs, 1 H), 7.52 (d, J = 7.7 Hz, 1 H), 7.25 (d, J = 7.1 Hz, 1 H), 7.25 (ddd, J = 1.3, 7.1, 7.9 Hz, 1 H), 7.05 (ddd, J = 1.2, 7.9, 7.7 Hz, 1 H), 6.55–6.33 (m, 2 H), 6.1–5.96 (m, 1 H), 1.91 (dd, J = 1.7, 6.7 Hz, 3 H). Anal. Calcd for $C_{11}H_{11}N$ (157.21): C, 84.04; H, 7.05; N, 8.89. Found: C, 83.85; H, 7.06; N, 9.05.

2-(Propen-2-yl)indole: mp 111.4–115 °C (hexane) [lit.[20] 118–120 °C]. Anal. Calcd for $C_{11}H_{11}N$ (157.21): C, 84.04; H, 7.05; N, 8.89. Found: C, 83.73; H, 7.05; N, 9.02.

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