A Direct Synthesis of 2-(Trimethylstannyl)pyrroles from Michael Acceptors and Stannylated Tosylmethyl Isocyanide[1]

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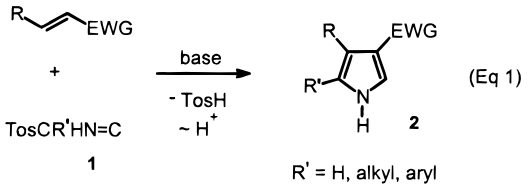
A series of 2-(trimethylstannyl)pyrroles **3**, with substituents at the 3- and 4-positions, is synthesized efficiently by a base-induced reaction of stannylated TosMIC with Michael acceptors. Stille cross-couplings with bromobenzene and double cross-couplings with 1,4-dibromobenzene have been achieved successfully with the *N*-methyl derivative (**5a**) and the *N*-Boc derivative (**6a**) of 3-benzoyl-2-(trimethylstannyl)-4-phenylpyrrole (**3a**), despite the bulk of these stannylpyrroles. Homo-coupling reactions of the same stannylpyrroles with the corresponding bromopyrroles (prepared from stannylpyrroles **3** and NBS) were unsuccessful, probably for steric reasons.

Introduction

In this paper, we report the first applications of a stannylated derivative of tosylmethyl isocyanide (TosMIC). The use of this new reagent is demonstrated by the synthesis of a series of 2-(trimethylstannyl)pyrroles **3**. This synthesis of pyrroles **3** has two novel characteristics: (1) the trimethylstannyl group in compounds **3** is not the result of a substitution onto a precursor-pyrrole, instead the stannyl group is introduced as part of the pyrrole ring-forming process; (2) stannylated pyrroles with a free *N*-H function have not been reported previously. Stannylated pyrroles such as **3** can be used, for example, in Stille cross-coupling reactions.[2]

So far, 2- and 3-stannylated pyrroles have been prepared only by reaction of 2- or 3-lithiopyrroles (prepared by direct lithiation or by halogen−lithium exchange) and Bu_3SnCl or Me_3SnCl. This stannylation procedure is possible only when the pyrrole nitrogen is substituted (protected).[3] *N*-Unprotected 2-stannylindoles have been reported recently as intermediates in the synthesis of 2,3-disubstituted (and 3-monosubstituted) indoles from *o*-isocyanostyrenes. In this interesting process, tributyltin radicals (from Bu_3SnH and AIBN) induce a ring closure in *o*-isocyanostyrenes to form 2-stannylindoles, which have been employed in the Stille reaction.[4]

TosMIC (**1**, R′ = H), and its substituted derivatives (**1**, R′ = alkyl/aryl), are being used extensively in the synthesis of 3,4-disubstituted and 2,3,4-trisubstituted pyrroles, respectively (eq 1). The substituent at position 4 is usually an electron-withdrawing group (EWG), originating from the Michael acceptor substrate.[5] With these results in mind, we decided to introduce a stannyl substituent in TosMIC, as in **1** with R′ = Me_3Sn, and to apply this synthon in the TosMIC-based pyrrole synthesis. This, according to expectations, should lead to pyrrole derivatives **2** with a Me_3Sn substituent in an apparently unequivocally determined position, according to eq 1.



(Eq 1)

So far, only a few (*N*-protected) 2-stannylpyrroles have been reported[6] and just one 3-stannylpyrrole: 3-(tri-*n*-butylstannyl)-1-(triisopropylsilyl)pyrrole.[7] These stannylpyrroles have been used almost exclusively in Stille coupling reactions.[2b] There is explicit interest in these Stille reactions for the synthesis of oligopyrroles, as a potential entry into conducting polypyrrole-polymers.[8]

Results and Discussion

Our first experiments were carried out with chalcone (*trans*-benzylideneacetophenone). The best results were obtained when TosMIC was reacted in THF at −75 °C with 2 equiv of *n*-BuLi (to form dilithio-TosMIC),[9] and then with excess of Me_3SnCl (2 equiv). Next, 1 equiv of chalcone was added at the same temperature. Workup provided one single (trimethylstannyl)pyrrole in 90% yield (Table 1, entry 1). Structure **2a** (R = Ph, R′ = Me_3Sn, EWG = PhCO) was assigned to this product initially, following eq 1. Much to our surprise, however, X-ray analysis of the *N*-Boc derivative unambiguously showed the product to be 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole (**3a**, eq 2, Table 1), rather than 4-benzoyl-3-phenyl-2-(trimethylstannyl)pyrrole (**2a**). X-ray analysis[10] became a necessity when the ^1H and ^{13}C NMR structure determination turned out not to be entirely unambiguous. The same approach was used to synthesize a series of analogous (trimethylstannyl)pyrroles **3** using other Michael acceptors (Table 1). In no case were indications found for the presence of a second, isomeric stannylpyrrole (of type **2**).

The actual ring-forming species of eq 2 has not been identified. It is, however, unlikely to be the anticipated

(1) Chemistry of Sulfonylmethyl Isocyanides. 45. For part 44, see: ten Have, R.; van Leusen, A. M. *Tetrahedron* **1998**, *54*, 1913.
(2) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1−652.
(3) See refs 2b, 6, 7, and 8.
(4) Fukuyama, T.; Chen, X.; Peng, G. *J. Am. Chem. Soc.* **1994**, *116*, 3127.

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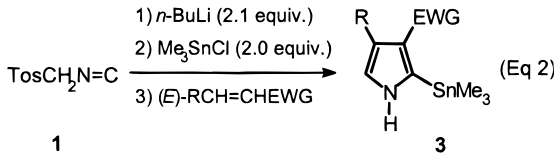
Table 1. 2-(Trimethylstannyl)pyrroles 3 from Michael Acceptors, TosMIC, and Me_3SnCl in a One-Pot Operation

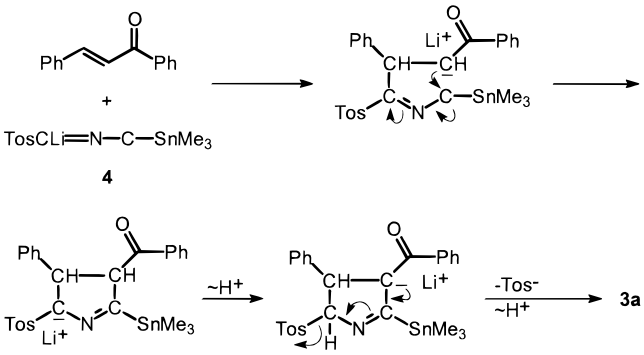


1 3

entry	R	EWG	product	yield (%)	mp (°C)
1	Ph	COPh	**3a**	90	174−175
2	Ph	COMe	**3b**	60[a]	80−87
3	Ph	CO_2Me	**3c**	68	169−170
4	Ph	CO_2Et	**3d**	70	134−135
5	Ph	CO_2Ph	**3e**	70	151−152
6	Ph	CN	**3f**	61	182−183
7	Ph	NO_2	**3g**	40	179−181
8	CO_2Me	CO_2Me	**3h**	64	oil
9	PhCH=CH	COMe	**3i**	*b*	
10	PhCH=CH	COPh	**3j**	*b*	

[a] Yield estimated from ^1H NMR, purification by column chromatography and crystallization not successful. [b] Impure product only, isolation by column chromatography and crystallization not successful.

Scheme 1. Proposed Mechanism for Formation of (Trimethylstannyl)pyrrole 3a



$TosCLi(SnMe_3)N{=}C$, since that would imply either an integral migration of the Me_3Sn group in **2a** to form **3a**, or a regioreversal of the usual Michael type addition−cyclization depicted in eq 1. We tentatively propose that the reacting species, formed in situ from dilithio-TosMIC and Me_3SnCl, be $TosCLi{=}NCSnMe_3 \leftrightarrow TosCLi{=}N^+{=}C^-SnMe_3$ (**4**). A cycloaddition of **4** to chalcone by a Michael type addition−cyclization as in Scheme 1 (in one step or two steps)[5] would explain the formation of **3a** in a straightforward manner. There is a certain resemblance with the formation of 3-benzoyl-2,4-diphenylpyrrole from chalcone and $TosCH_2N{=}C(SMe)Ph$ using NaH. In this process, the TosMIC-isocyano carbon bears two substituents, of which the SMe is lost in the pyrrole ring formation.[11]

The yield of pyrrole **3a** was lowered from 90% (Table 1, entry 1) to 80% when the excess of Me_3SnCl was reduced from 2 to 1.2 equiv. A much lower yield of **3a** was obtained when an attempt was made to prepare the stannylated TosMIC derivative **4** in a different way: subsequent reaction of TosMIC in THF at −75 °C with 1 equiv of *n*-Buli, then Me_3SnCl (2 equiv), followed by a second equivalent of *n*-BuLi and by chalcone gave **3a** in less than 5% yield. Presumably, the reacting species **4** is formed only in an efficient manner from the stronger nucleophilic dilithio-TosMIC[9] and (excess) Me_3SnCl. The corresponding reaction of *n*-Bu_3SnCl with TosMIC and chalcone did not lead to the tributylstannyl analogue of **3a**, possibly due to steric overcrowding.

Scheme 3 shows some applications of the newly formed (trimethylstannyl)pyrroles **3**, of which the Stille reaction[2] is the most obvious one. In as much as the Stille reaction has been applied to pyrroles, only *N*-substituted (protected) stannylpyrroles have been used.[6−8,12] We have prepared both the *N*-Me and the *N*-Boc derivatives of **3a** by two methods (Scheme 2, Table 2). First of all, (trimethylstannyl)pyrrole **3a** was *N*-methylated with MeI under PTC conditions to give **5a** in 86% yield; the *N*-Boc group was introduced in **3a** with the use of Boc_2O to give **6a** in 79% yield (Method 1; Table 2, entries 1 and 2, respectively). The same compounds were also prepared in the "classical" way from 3-benzoyl-1-methyl-3-phenylpyrrole (**8**) and 3-benzoyl-1-(*tert*-butoxycarbonyl)-3-phenylpyrrole (**9**), via *ortho*-litiation using lithium 2,2,6,6-tetramethylpiperidide (LTMP), to give **5a** and **6a** in 72 and 79% yields, respectively (Method 2; Table 2, entries 1 and 2). Method 2 was also used to prepare the corresponding (trimethylstannyl)pyrroles **5j** and **6j** (Table 2, entries 3 and 4, respectively).

Although the overall yields of **5a** and **6a** from chalcone by the two methods may be comparable, Method 2 requires three steps and Method 1 two. Furthermore, the *ortho*-lithiation step of Method 2 appears not to be site-specific in all cases. Whereas Method 2 gave single pyrroles **5a**, **5j**, and **6a** from **8a**, **8j**, and **9a**, respectively, in case of $R^1 = Ph$, the corresponding reaction with $R^1 =$

(5) Some references are as follows: (a) Possel, O.; van Leusen, A. M. *Heterocycles* **1977**, *7*, 77. (b) Moskal, J.; van Leusen, A. M. *J. Org. Chem.* **1986**, *51*, 4131. (c) Magnus, P.; Gallagher, T.; Schultz, J.; Or, Y.-S.; Ananthanarayan, T. P. *J. Am. Chem. Soc.* **1987**, *109*, 2706. (d) van Leusen, D.; Flentge, E.; van Leusen, A. M. *Tetrahedron* **1991**, *47*, 4639. (e) van Leusen, D.; van Echten, E.; van Leusen, A. M. *J. Org. Chem.* **1992**, *57*, 2245. (f) Dell'Erba, C.; Giglio, A.; Mugnoli, A.; Novi, M.; Petrillo, G.; Stagnaro, P. *Tetrahedron* **1995**, *51*, 5181. (g) van Leusen, A. M.; van Leusen, D. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 7, p 4973. (h) van Leusen, A. M.; van Leusen, D. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995, Vol. 5, p 3605. (i) ten Have, R.; Leusink, F. R.; van Leusen, A. M. *Synthesis* **1996**, 871. For an exhaustive account, see: (j) van Leusen, D.; van Leusen, A. M. *Org. React.*, in press.

(6) The first stannylated pyrrole, 1-(dimethylamino)-2-(trimethylstannyl)pyrrole, was reported in 1981: Martinez, G. R.; Grieco, P. A.; Srinivasan, C. V. *J. Org. Chem.* **1981**, *46*, 3760. The first application in a Stille cross-coupling (of 1-methyl-2-(trimethylstannyl)pyrrole) dates from 1986: Bailey, T. R. *Tetrahedron Lett.* **1986**, *27*, 4407.

(7) Alvarez, A.; Guzman, A.; Ruiz, A.; Velarde, E.; Muchowski, J. M. *J. Org. Chem.* **1992**, *57*, 1653.

(8) Leading references: Zerbi, G.; Veronelli, M.; Martina, S.; Schlüter, A.-D.; Wegner, G. *Adv. Mater.* **1994**, *6*, 315. Groenendaal, L.; Peerlings, H. W. I.; Havinga, E. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Synth. Metals* **1995**, *69*, 467. Groenendaal, L. Ph.D. Thesis, Eindhoven (The Netherlands), 1996. Wang, J.; Scott, A. I. *Tetrahedron Lett.* **1996**, *37*, 3247.

(9) van Nispen, S. P. J.; Mensink, C.; van Leusen, A. M. *Tetrahedron Lett.* **1980**, *21*, 3723.

(10) The X-ray structure of the *N*-Boc derivative of **3a** was published elsewhere: Meetsma, A.; Dijkstra, H. P.; ten Have, R.; van Leusen, A. M. *Acta Crystallogr.* **1996**, *C52*, 2747. This paper, which also describes the nonoptimized synthesis of **3a** and its *N*-Boc derivative, is to be considered the preliminary of the present paper.

(11) Houwing, H. A.; van Leusen, A. M. *J. Heterocycl. Chem.* **1981**, *18*, 1127, and ref 5h. Furthermore, for the use of Pd, Pt, and W complexes of isocyanides, see: Fehlhammer, W. P.; Bartel, K.; Völkl, A.; Achatz, D *Z. Naturforsch.* **1982**, *37b*, 1044.

(12) The limitation of the Stille reaction to *N*-substituted (protected) pyrroles probably has more to do with the preparation of the stannylpyrroles[3] than with the Stille reaction itself. As a matter of fact many functional groups are compatible with the Stille reaction. In the many applications of the Stille reaction to indoles, *N*-substituted (protected) indoles were used, with one recent exception.[2] This one exception[4] may be seen as an indication that the Stille reaction of *N*-unprotected pyrroles ought to be possible too.

Scheme 2. Two Approaches to *N*-Protected (Trimethylstannyl)pyrroles 5 and 6

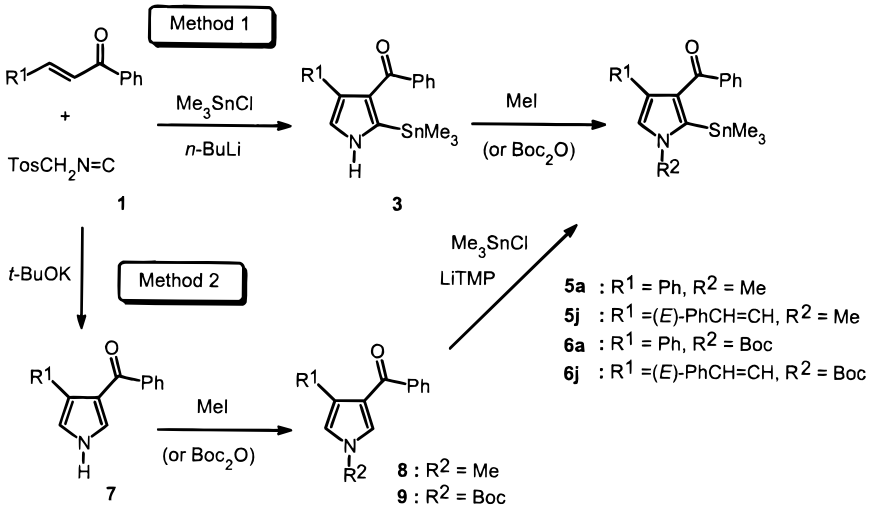
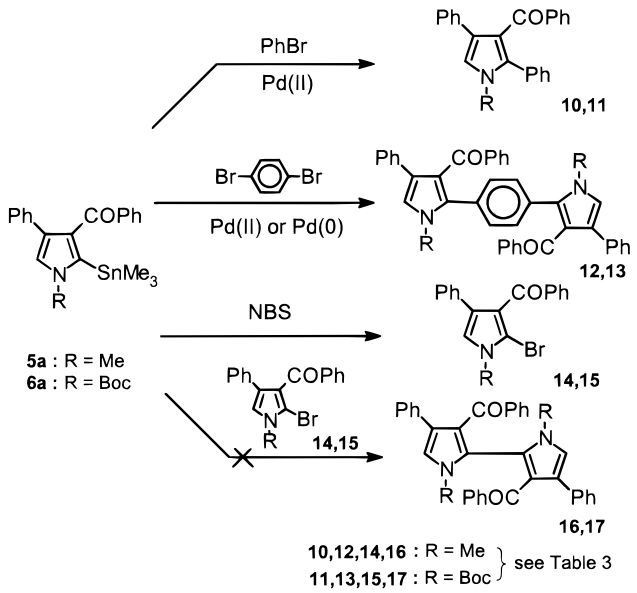


Table 2. Pyrroles 7, 8, and 9 and (Trimethylstannyl)pyrroles 5 and 6 According to Scheme 2

entry	R^1	compd[a]	yield (%)	mp (°C)	compd	R^2	yield (%)	mp (°C)	compd	yield (%)	mp (°C)
1	Ph	**7a**	70	229−231	**8a**	Me	92	oil	**5a**	86[b]/72[c]	103−105
2					**9a**	Boc	78	129−131	**6a**	79[b]/79[c]	122−123
3	(*E*)-PhCH=CH	**7j**	98	172−175	**8j**	Me	54	109−110	**5j**	74	146−148
4					**9j**	Boc	81	130−132	**6j**	60[d]	

[a] For starting material **3a**, see Table 1. [b] Yield by using Method 1. [c] Yield by using Method 2. [d] Mixture of two isomers (see text and Experimental Section).

Scheme 3. Some Applications of Stannylpyrroles 5a and 6a



(*E*)-PhCH=CH not only gave **6j** but also the isomeric 4-benzoyl-1-(*tert*-butoxycarbonyl)-3-(2-phenylethenyl)-2-trimethylstannylpyrrole (**6j′**) (ratio 1.2:1 or 1:1.2, see Experimental Section). Unfortunately, we have been unable to compare the results of entries 3 and 4 by Method 2 with Method 1, since **3j** was not obtained in pure state.

Scheme 3 and Table 3 show some reactions of stannylpyrroles **5a** and **6a**. The Stille cross-coupling with bromobenzene to the 2-phenylpyrroles **10** and **11** took place in 65 and 71% yields, respectively. The yields of the double cross-coupling with 1,4-dibromobenzene to **12** and **13** were lower (25 and 21%, respectively). The homocoupling reactions of **5a** and **6a** with the corresponding

Table 3. (Trimethylstannyl)pyrroles 5a and 6a Applied in the Stille Reaction and in NBS Bromination

entry	R	product	yield (%)	mp (°C)
1	Me	**10**	65	120−122
2	Boc	**11**	71	92−93
3	Me	**12**	50	295−296
4	Boc	**13**	21	*a*
5	Me	**14**	87	107−108
6	Boc	**15**	75	oil
7	Me	**16**	*b*	
8	Boc	**17**	*b*	

[a] Decomposition at ca. 190 °C. [b] Reaction unsuccessful (see text).

2-bromopyrroles **14** and **15** were unsuccessful, possibly as a result of steric overcrowding. The bromopyrroles **14** and **15** were obtained by replacement of the Me_3Sn group in **5a** and **6a**, in 87 and 75% yields, respectively, with *N*-bromosuccinimide (NBS).

Primarily as additional evidence of the structure of compounds **3**, 3-benzoyl-2,4-diphenyl-1-methylpyrrole (**10**) was prepared independently by *N*-methylation of 3-benzoyl-2,4-diphenylpyrrole.[11] The two samples were identical by ^{1}H NMR. 4-Benzoyl-1-methyl-2,3-diphenylpyrrole (**18**), isomeric with **10**, was prepared by reaction of chalcone with 1-tosylbenzyl isocyanide[17] followed by *N*-methylation (see Experimental Section).

Experimental Section

All experiments, with the exception of the *N*-methylation reactions, were carried out in a dry nitrogen atmosphere. The Michael acceptors used in the preparation of **3a**, **3b**, **3c**, **3d**,

(13) Fuson, T. C.; Thomas, N. *J. Org. Chem.* **1953**, *18*, 1762.
(14) Worall, D. E. *Organic Syntheses*; Wiley: New York, 1947; Collect. Vol. I, p 413.
(15) Diehl, L.; Einhorn, A. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2320.
(16) Thomas, J. F.; Branch, G. *J. Am. Chem. Soc.* **1953**, *75*, 4793.
(17) van Leusen, A. M.; Siderius, H.; Hoogenboom, B. E.; van Leusen, D. *Tetrahedron Lett.* **1972**, 5337.

3f, **3h**, trimethylstannyl chloride, bis(triphenylphosphine)-palladium(II) chloride, and tetrakis(triphenylphosphine)-palladium(0) are commercial products (Aldrich), which have been used as received. The Michael acceptors used for the preparation of **3e,**[13] **3g**,[14] **3i**,[15] and **3j**[16] were prepared according to the literature procedures indicated. Tosylmethyl isocyanide (TosMIC), purchased from Ofichem (Ter Apel, The Netherlands), was chromatographed (Al_2O_3, CH_2Cl_2) before use. Column chromatographies were performed on basic alumina (Brockmann 90, II/III 0.063−0.200 mm) or on neutral alumina (aluminum oxide 90, activity I, Merck) using CH_2Cl_2 as eluent. CH_2Cl_2 was distilled over P_2O_5 before use. THF was distilled from Na wire. Melting points are uncorrected. ^{1}H NMR spectra were recorded at 500, 300, or 200 MHz. ^{1}H NMR chemical shifts were determined relative to the solvent and were converted to the TMS scale using $\delta(CHCl_3) = 7.26$. ^{13}C NMR spectra were recorded at 125.7, 75.4, or 50.4 MHz. ^{13}C NMR chemical shifts were determined relative to the solvent and were converted to the TMS scale using $\delta(CDCl_3) = 76.91$. ^{119}Sn NMR spectra were recorded at 186.4 or 111.9 MHz. ^{119}Sn NMR chemical shifts were determined relative to Me_3SnCl and were converted to the TMS scale using $\delta(Me_3SnCl) = 167.4$.

3-Benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole (3a). Typical Procedure. *n*-BuLi (1.6 M in *n*-hexane, 2.6 mL, 4.2 mmol) was added to a solution of TosMIC (0.39 g, 2.0 mmol) in THF (30 mL) at −75 °C. After 5 min of stirring at −75 °C, Me_3SnCl (0.80 g, 4.0 mmol) in THF (5 mL) was added dropwise. After another 5 min of stirring at −75 °C, a solution of chalcone (0.42 g, 2.0 mmol) in THF (5 mL) was added dropwise. The temperature of the reaction mixture was allowed to rise to room temperature in 30 min, and stirring was continued for 2 h. Water (50 mL) was added, and the mixture was extracted with Et_2O (3 × 50 mL). The combined extracts were washed with water and with brine, dried ($MgSO_4$), and concentrated. The solid residue was filtered through a short (1 cm) column of neutral alumina (CH_2Cl_2) to give, after removal of the solvent, 0.74 g (90%) of compound **3a** as a white solid, which was analytically pure, mp 174−175 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.37 (s, 9H), 6.97−7.26 (m, 9H), 7.50 (d, J = 1.5 Hz, 1H), 7.52 (d, J = 4.9 Hz, 1H), 8.69 (br, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −8.7 (q), 121.4 (d), 122.5 (s), 125.5 (d), 127.2 (d), 127.5 (d), 127.9 (s), 128.9 (d), 129.3 (d), 131.0 (d), 135.1 (s), 139.0 (s), 142.7 (s), 194.3 (s); ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −59.2; MS (relative intensity, %) *m*/*z* 28 (29.6), 77 (22.6), 105 (15.4), 170 (22.1), 247 (19.2), 364 (15.0), 396 (100.0), 411 (M^+, 0.7); HRMS *m*/*z* calcd for $C_{20}H_{21}NOSn$ 411.065, found 411.065. Anal. Calcd for $C_{20}H_{21}NOSn$: C, 58.38; H, 5.15; N, 3.41; Sn, 29.17. Found: C, 58.42; H, 5.11; N, 3.34; Sn, 28.96.

3-Acetyl-4-phenyl-2-(trimethylstannyl)pyrrole (3b). Following the procedure decribed for **3a**, (*E*)-4-phenyl-3-buten-2-one (0.29 g, 2.0 mmol) was stirred for 2 h while the temperature of the reaction mixture was kept below −30 °C. After workup a mixture (0.61 g, mp 80−87 °C) was obtained, which consisted of **3b** (about 60% based on ^{1}H NMR), TosMIC, and other unidentified compounds. Purification by column chromatography and crystallization did not succeed: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.32 (s, 9H), 2.02 (s, 3H), 6.92 (d, J = 2.4 Hz, 1H), 7.37 (s, 5H), 8.58 (br, 1H).

3-Methoxycarbonyl-4-phenyl-2-(trimethylstannyl)pyrrole (3c). Following the procedure described for **3a**, methyl *trans*-cinnamate (0.32 g, 2.0 mmol) gave analytically pure **3c** as a white solid (0.50 g, 68%): mp 169−170 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.37 (s, 9H), 3.72 (s, 3H), 6.95 (d, J = 2.4 Hz, 1H), 7.24−7.51 (m, 5H), 8.53 (br, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −8.6 (q), 50.4 (q), 120.8 (s), 122.2 (d), 126.2 (d), 127.5 (d), 128.0 (s), 129.3 (d), 135.2 (s), 142.0 (s), 166.1 (s); ^{119}Sn NMR ($CDCl_3$, 111.9 MHz) δ −57.2; MS (relative intensity, %) *m*/*z* 28 (44.8), 32 (11.5), 170 (12.3), 288 (17.3), 318 (34.1), 350 (100.0), 365 (M^+, 4.3); HRMS *m*/*z* calcd for $C_{15}H_{19}NO_2Sn$ 365.044, found 365.044. Anal. Calcd for $C_{15}H_{19}NO_2Sn$: C, 49.31; H, 5.25; N, 3.84; Sn, 32.85. Found: C, 49.33; H, 5.28; N, 3.81; Sn, 32.71.

3-Ethoxycarbonyl-4-phenyl-2-(trimethylstannyl)pyrrole (3d). Following the procedure described for **3a**, ethyl *trans*-cinnamate (0.35 g, 2.0 mmol) gave, after being washed with dry pentane, analytically pure **3d** as a white solid (0.53 g, 70%): mp 134−135 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.37 (s, 9H), 1.20 (t, 3H), 4.21 (q, 2H), 6.95 (d, J = 2.2 Hz, 1H), 7.23−7.49 (m, 5H), 8.49 (br, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −8.6 (q), 14.0 (q), 59.5 (t), 121.4 (s), 122.1 (d), 126.2 (d), 127.3 (d), 127.9 (s), 129.4 (d), 135.4 (s), 141.6 (s), 166.1 (s); ^{119}Sn NMR ($CDCl_3$, 111.9 MHz) δ −57.7; MS (relative intensity, %) *m*/*z* 28 (66.9), 159 (11.0), 170 (11.8), 288 (17.5), 318 (35.4), 334 (12.0), 364 (100.0), 379 (M^+, 4.6); HRMS *m*/*z* calcd for $C_{16}H_{21}NO_2Sn$ 379.059, found 379.059. Anal. Calcd for $C_{16}H_{21}NO_2Sn$: C, 50.84; H, 5.60; N, 3.71; Sn, 31.40. Found: C, 50.75;H, 5.61; N, 3.69; Sn, 31.30.

3-Phenoxycarbonyl-4-phenyl-2-(trimethylstannyl)pyrrole (3e). Following the procedure described for **3a**, phenyl *trans*-cinnamate[13] (0.48 g, 2.0 mmol) gave analytically pure **3e** as a white solid (0.60 g, 70%): mp 151−152 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.37 (s, 9H), 7.02−7.55 (m, 11H), 8.55 (br, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −8.6 (q), 120.0 (s), 121.7 (d), 122.2 (d), 125.0 (d), 126.1 (d), 127.3 (d), 128.5 (s), 129.0 (d), 129.1 (d), 134.7 (s), 143.0 (s), 150.3 (s), 163.9 (s); ^{119}Sn NMR ($CDCl_3$, 111.9 MHz) δ −52.9; MS (relative intensity, %) *m*/*z* 28 (56.6), 94 (18.9), 120 (12.9), 170 (31.1), 288 (20.8), 304 (27.1), 318 (25.8), 334 (100.0), 412 (88.9), 427 (M^+, 1.3); HRMS *m*/*z* calcd for $C_{20}H_{21}NO_2Sn$ 427.059, found 427.059. Anal. Calcd for $C_{20}H_{21}NO_2Sn$: C, 56.38; H, 4.97; N, 3.29; Sn, 27.86. Found: C, 56.41; H, 5.05; N, 3.30; Sn, 27.52.

3-Cyano-4-phenyl-2-(trimethylstannyl)pyrrole (3f). Following the procedure described for **3a**, cinnamonitrile (0.26 g, 2.0 mmol) gave, after one crystallization from CH_2Cl_2, analytically pure **3f** as a white solid (0.40 g, 61%): mp 182−183 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.48 (s, 9H), 7.14 (d, J = 2.4 Hz, 1H), 7.26−7.66 (m, 5H), 8.64 (br, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −8.2 (q), 101.5 (s), 119.5 (s), 120.5 (d), 127.4 (d), 127.7 (d), 129.3 (s), 129.5 (d), 133.7 (s), 143.4 (s); ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −45.8; MS (relative intensity, %) *m*/*z* 28 (74.6), 115 (15.7), 120 (15.8), 140 (12.0), 168 (21.6), 287 (36.1), 317 (100.0), 332 (M^+, 32.8); HRMS *m*/*z* calcd for $C_{14}H_{16}N_2Sn$ 332.033, found 332.033. Anal. Calcd for $C_{14}H_{16}N_2Sn$: C, 50.60; H, 4.86; N, 8.43; Sn, 36.11. Found: C, 50.73; H, 4.87; N, 8.40; Sn, 35.96.

3-Nitro-4-phenyl-2-(trimethylstannyl)pyrrole (3g). Following the procedure described for **3a**, β-nitrostyrene[14] (0.30 g, 2.0 mmol) gave, after filtration through a short (4 cm) column of neutral Al_2O_3 (CH_2Cl_2), analytically pure **3g** as a yellow solid (0.28 g, 40%): mp 179−181 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.42 (s, 9H), 6.88 (d, J = 2.4 Hz, 1H), 7.26−7.46 (m, 5H), 8.54 (br, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −8.9 (q), 122.5 (d), 123.0 (s), 127.1 (d), 127.8 (d), 129.2 (d), 132.7 (s), 140.2 (s); ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −48.6; MS (relative intensity, %) *m*/*z* = 28 (47.6), 32 (12.3), 307 (16.7), 337 (100.0), 352 (M^+, 1.1); HRMS *m*/*z* calcd for $C_{13}H_{16}N_2O_2Sn$ 352.023, found 352.023. Anal. Calcd for $C_{13}H_{16}N_2O_2Sn$: C, 44.32; H, 4.58; N, 7.96; Sn, 34.06. Found: C, 44.35; H, 4.62; N, 7.86; Sn, 33.83.

3,4-Dimethoxycarbonyl-2-(trimethylstannyl)pyrrole (3h). Following the procedure described for **3a**, dimethyl fumarate (0.72 g, 5.0 mmol) gave, after filtration through a short (4-cm) column of neutral Al_2O_3 (CH_2Cl_2), **3h** as a brown oil (1.1 g, 64%), pure according to ^{1}H NMR. **3h**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.33 (s, 9H), 3.81 (s, 3H), 3.82 (s, 3H), 7.49 (s, 1H), 8.63 (br, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −8.7 (q), 51.0 (q), 51.3 (q), 116.7 (s), 122.8 (s), 128.9 (d), 143.0 (s), 164.8 (s), 165.4 (s); ^{119}Sn NMR ($CDCl_3$, 111.9 MHz) δ −53.9; MS (relative intensity, %) *m*/*z* 44 (8.8), 136 (8.4), 149 (13.5), 151 (14.3), 270 (23.9), 300 (100), 332 (M^+ − Me, 88.1); HRMS *m*/*z* calcd for $C_{10}H_{14}NO_4Sn$ 331.9945, found 331.9920.

Attempted Synthesis of (*E*)-3-Acetyl-4-(2-phenylethenyl)-2-(trimethylstannyl)pyrrole (3i). Following the procedure described for **3a**, (*E*,*E*)-6-phenyl-3,5-hexadien-2-one[15] (0.34 g, 2.0 mmol) gave a yellow foam (0.75 g), which according to ^{1}H NMR consisted of mixture of **3i** and other unidentified compounds. Purification by column chromatography and crystallization was unsuccessful.

Attempted Synthesis of (*E*)-3-Benzoyl-4-(2-phenylethenyl)-2-(trimethylstannyl)pyrrole (3j). Following the procedure described for **3a**, (*E*,*E*)-1,5-diphenyl-2,4-pentadien-1-one[16] (0.47 g, 2.0 mmol) gave a pale yellow oil, which according to ^{1}H NMR consisted of a mixture of **3j**, starting material, and other unidentified compounds. Purification by column chromatography and crystallization was unsuccessful.

3-Benzoyl-1-methyl-4-phenyl-2-(trimethylstannyl)pyrrole (5a). Method 1. KOH (50% in water, 3 mL) was added to a solution of 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole (**3a**, 0.41 g, 1.0 mmol), CH_3I (0.5 mL, 8 mmol), and benzyltriethylammonium chloride (25 mg, 0.15 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h; then water (20 mL) was added. The organic layer was separated, dried ($MgSO_4$), and concentrated to give **5a** as a white solid (0.37 g, 86%). Crystallization from petroleum ether (bp 40−60 °C) gave white crystals, mp 103−105 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.27 (s, 9H), 3.71 (s, 3H), 6.76 (s, 1H), 6.87−7.16 (m, 8H), 7.42−7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −6.0 (q), 38.7 (q), 125.3 (d), 126.2 (d), 127.2 (d), 127.5 (d), 128.8 (d), 129.5 (d), 131.0 (d), 131.9 (s), 135.0 (s), 139.0 (s), 143.8 (s), 178.4 (s), 194.1 (s); ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −65.8; MS (relative intensity, %) *m*/*z* 57 (12.1), 69 (10.3), 77 (7.8), 105 (6.4), 115 (5.3), 129 (6.3), 184 (47.6), 205 (7.9), 244 (15.2), 261 (43.9), 380 (26.7), 410 (M^+, 100); HRMS *m*/*z* calcd for $C_{20}H_{20}NOSn$ 410.0567, found 410.0557. Anal. Calcd for $C_{20}H_{20}NOSn$: C, 59.47; H, 5.47; N, 3.30; Sn, 27.99. Found: C, 59.44; H, 5.46; N, 3.36, Sn, 27.94. **Method 2.** *n*-BuLi (1.6 M in *n*-hexane, 16.1 mL, 25.7 mmol) was added dropwise to 2,2,6,6-tetramethylpiperidine (3.31 g, 23.4 mmol) in THF (100 mL) at −80 °C. The solution was allowed to warm to 0 °C and was kept at that temperature for 10 min. The solution was cooled again to −80 °C, and a solution of 3-benzoyl-1-methyl-4-phenylpyrrole (**8a**, 5.57 g, 21.3 mmol, see below) in THF (50 mL) was added dropwise. After another 15 min of stirring at −80 °C, a solution of Me_3SnCl (4.66 g, 23.4 mmol) in THF (25 mL) was added dropwise. The mixture was stirred for 30 min at the same temperature and for another 60 min while the temperature was allowed to rise to −10 °C. The reaction mixture was poured into water (75 mL), and the solution was extracted with Et_2O (2 × 75 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), concentrated, and filtered through a short column of neutral Al_2O_3 (CH_2Cl_2). The eluent was concentrated, and the pale brown solid was crystallized from petroleum ether (bp 40−60 °C) to give **5a** as a white solid (6.5 g, 72%), which was identical to the above material according to ^{1}H NMR.

(*E*)-3-Benzoyl-1-methyl-4-(2-phenylethenyl)-2-(trimethylstannyl)pyrrole (5j). Following the procedure described for **5a** (Method 2), (*E*)-3-benzoyl-1-methyl-4-(2-phenylethenyl)-pyrrole (**8j**, 0.86 g, 3.0 mmol, see below), 2,2,6,6-tetramethylpiperidine (0.47 g, 3.3 mmol), *n*-BuLi (1,6 M in *n*-hexane, 2.3 mL, 3.6 mmol), and Me_3SnCl (0.66 g, 3.3 mmol) gave **5j** as a yellow solid (1.0 g, 74%). Crystallization from Et_2O gave **5j** as pale yellow crystals: mp 146−148 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.36 (s, 9H), 3.79 (s, 3H), 6.40 (d, J = 16.1 Hz, 1H), 6.58 (d, J = 16.4 Hz, 1H), 7.00−7.28 (m, 6H), 7.40−7.55 (m, 3H), 7.75−7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −6.0 (q), 38.9 (q), 121.7 (d), 123.8 (s), 124.8 (d), 125.6 (d), 125.9 (d), 126.5 (d), 128.0 (d), 128.3 (d), 129.3 (d), 131.4 (d), 132.3 (s), 137.8 (s), 140.5 (s), 144.1 (s), 193.7 (s); ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −63.1; MS (relative intensity, %) *m*/*z* 77 (8.7), 105 (8.0), 167 (5.9), 182 (17.0), 210 (17.0), 287 (50.7), 406 (17.6), 436 (100), 451 (M^+, 3.0); HRMS *m*/*z* calcd for $C_{23}H_{25}NOSn$ 451.0958, found 451.0996. Anal. Calcd for $C_{23}H_{25}NOSn$: C, 61.18; H, 5.59; N, 3.16; Sn, 26.58. Found: C, 61.41; H, 5.59; N, 3.14; Sn, 26.42.

3-Benzoyl-1-(*tert*-butoxycarbonyl)-4-phenyl-2-(trimethylstannyl)pyrrole (6a). Method 1. 3-Benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole (**3a**, 0.82 g, 2.0 mmol), di-*tert*-butyl dicarbonate (0.48 g, 2.2 mmol), and *t*-BuOK (0.11 g, 1.0 mmol) in THF (40 mL) were refluxed for 1 h. The reaction mixture was quenched with water (25 mL) and was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. The crude product was filtered through a short column of neutral Al_2O_3 (CH_2Cl_2). The eluent was concentrated, and the product was crystallized from petroleum ether (bp 40−60 °C) to give **6a** as white crystals (0.81 g, 79%): mp 115−117 °C (lit.[10] mp 118−119 °C). Analytically pure **6a** was obtained by crystallization from CH_2Cl_2: mp 122−123 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9H), 1.63 (s, 9H), 7.09−7.50 (m, 9H), 7.85−7.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −6.1 (q), 27.8 (q), 84.4 (s), 121.2 (d), 126.5 (d), 127.8 (d), 128.0 (d), 128.1 (d), 129.1 (s), 130.1 (d), 132.8 (d), 133.6 (s), 135.9 (s), 138.3 (s), 150.1 (s), 195.2 (s); ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −49.9; MS (relative intensity, %) *m*/*z* 57 (16.6), 77 (4.9), 105 (9.0), 149 (13.0), 167 (7.5), 279 (5.6), 366 (9.5), 440 (100), 496 (M^+ − Me, 22.7); HRMS *m*/*z* calcd for $C_{25}H_{29}NO_3Sn$ 496.0935, found 496.0935. Anal. Calcd for $C_{25}H_{29}NO_3Sn$: C, 58.69; H, 5.72; N, 2.74; Sn, 23.46. Found: C, 58.74; H, 5.62;N, 2.79; Sn, 23.35. **Method 2.** *n*-BuLi (1.6 M in *n*-hexane, 9.8 mL, 15.7 mmol) was added dropwise to 2,2,6,6-tetramethylpiperidine (2.0 g, 14.3 mmol) in THF (100 mL) at −80 °C. The yellow solution was allowed to warm to 0 °C and was kept at that temperature for 10 min. The solution was cooled again to −80 °C, and a solution of 3-benzoyl-1-(*tert*-butoxycarbonyl)-4-phenylpyrrole (**9a**, 4.5 g, 3.0 mmol, see below) in THF (50 mL) was added dropwise. After another 30 min of stirring at −80 °C, a solution of Me_3SnCl (2.84 g, 14.3 mmol) in THF (25 mL) was added. The mixture was stirred for 30 min at the same temperature and then another 30 min while the temperature was allowed to rise to room temperature. The reaction was poured into water (75 mL) and extracted with Et_2O (2 × 75 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), concentrated, and filtered through a short column of neutral Al_2O_3 (CH_2Cl_2). The eluent was concentrated to give **6a** as a pale yellow solid (5.25 g, 79%), pure according to ^{1}H NMR. This material was identical by ^{1}H NMR and ^{13}C NMR with the compound prepared by Method 1.

(*E*)-3-Benzoyl-1-(*tert*-butoxycarbonyl)-4-(2-phenylethenyl)-2-(trimethylstannyl)-pyrrole (6j) and (*E*)-4-Benzoyl-1-(*tert*-butoxycarbonyl)-3-(2-phenylethenyl)-2-(trimethylstannyl)pyrrole (6j′). Following the procedure described for **6a** (Method 2), 3-benzoyl-1-(*tert*-butoxycarbonyl)-4-(2-phenylethenyl)pyrrole (**9j**, 1.87 g, 5.0 mmol, see below), 2,2,6,6-tetramethylpiperidine (0.77 g, 5.5 mmol), *n*-BuLi (1,6 M in *n*-hexane, 3.8 mL, 6.05 mmol), and Me_3SnCl (1.1 g, 5.5 mmol) gave a red oil (1.6 g, 60%) which contained a mixture of two stannylated pyrroles **6j** and **6j′** in a ratio of 1:1.2 or 1.2:1, as was established by ^{119}Sn NMR of the mixture. ^{119}Sn NMR ($CDCl_3$, 186.4 MHz) δ −49.8 and −51.3.

3-Benzoyl-4-phenylpyrrole[17] (7a). TosMIC (6.0 g, 31 mmol) in THF (40 mL) was added dropwise to a stirred solution of *t*-BuOK (3.7 g, 33 mmol) in THF (125 mL) at −80 °C. After 10 min of stirring at −80 °C, a solution of chalcone (6.3 g, 30 mmol) in THF (40 mL) was added dropwise. The reaction mixture was stirred for 90 min while the temperature was allowed to rise to room temperature. The reaction mixture was poured into ice/water (300 mL), and the solid was collected by filtration to give **7a** as a pale yellow solid (6.4 g, 86%), pure according to ^{1}H NMR: mp 228−229 °C (lit.[17] yield 70%, mp 229−231 °C); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.07−7.74 (m, 12 H), 11.63 (br, 1H); ^{13}C NMR (DMSO-d_6, 75.4 MHz) δ 119.6 (d), 120.6 (s), 125.5 (s), 125.6 (d), 127.7 (d), 128.1 (d), 128.2 (d), 128.4 (d), 128.9 (d), 131.5 (d), 135.2 (s), 140.0 (s), 190.4 (s); MS (relative intensity, %) *m*/*z* 77 (7.8), 115 (22.2), 142 (9.6), 170 (96.5), 218 (11.1), 247 (M^+, 100); HRMS *m*/*z* calcd for $C_{17}H_{13}NO$ 247.0997, found 247.0999. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.30; H, 5.33; N, 5.65.

(*E*)-3-Benzoyl-4-(2-phenylethenyl)pyrrole (7j). TosMIC (5.9 g, 30 mmol) in THF (50 mL) was added dropwise to a stirred solution of *t*-BuOK (6.8 g, 61 mmol) in THF (100 mL) at −80 °C. After 10 min of stirring at −80 °C, a solution of (*E*,*E*)-1,5-diphenyl-2,4-pentadien-1-one[16] (5.4 g, 28 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred for 1 h while the temperature was allowed to rise to room temperature. The reaction mixture was poured into ice/water (400 mL), and the solid was collected by filtration to

give **7j** as a pale yellow solid (6.7 g, 98%), pure according to ^{1}H NMR: mp 172−175 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.83 (d, J = 16.5 Hz, 1H), 7.03−7.47 (m, 10H), 7.61 (d, J = 16.5 Hz, 1H), 7.70−7.73 (m, 2H), 8.65 (br, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 116.6 (d), 121.4 (d), 121.9 (s), 124.4 (s), 126.2 (d), 126.9 (d), 127.4 (d), 127.6 (d), 128.1 (d), 128.4 (d), 129.0 (d), 131.4 (d), 137.9 (s), 140.4 (s), 192.1 (s); MS (relative intensity, %) *m*/*z* 77 (9.4), 105 (8.2), 139 (6.0), 168 (28.7), 196 (33.0), 244 (9.0), 256 (5.7), 273 (M^+, 100); HRMS *m*/*z* calcd for $C_{19}H_{15}NO$ 273.1154, found 273.1173. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.11; H, 5.55; N, 5.09.

3-Benzoyl-1-methyl-4-phenylpyrrole (8a). A solution of KOH (50% in water, 75 mL) was added to a solution of 3-benzoyl-4-phenylpyrrole (**7a**, 6.18 g, 25.0 mmol), benzyltriethylammonium chloride (2.0 g, 8.8 mmol), and MeI (6.2 mL, 100 mmol) in CH_2Cl_2 (100 mL). The suspension was stirred vigorously for 1 h. Water (75 mL) was added to the clear reaction mixture, and the organic layer was separated, dried ($MgSO_4$), and filtered through a short column of basic Al_2O_3 (CH_2Cl_2). The eluent was concentrated to give **8a** as a pale yellow oil (6.0 g, 92%), pure according to ^{1}H NMR. **8a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.70 (s, 3H), 6.74 (d, J = 2.6 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 7.20−7.48 (m, 8H), 7.79−7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 36.5 (q), 121.6 (s), 122.4 (d), 126.1 (d), 127.5 (s), 127.8 (d), 128.5 (d), 129.3 (d), 130.4 (d), 131.3 (d), 134.5 (s), 139.9 (s), 190.9 (s); MS (relative intensity, %) *m*/*z* 57 (6.5), 77 (7.5), 115 (8.4), 129 (10.2), 184 (100), 232 (7.3), 244 (7.3), 261 (M^+, 75.1); HRMS *m*/*z* calcd for $C_{18}H_{15}NO$ 261.1154, found 261.1165.

(*E*)-3-Benzoyl-1-methyl-4-(2-phenylethenyl)pyrrole (8j). Following the procedure described for **8a**, (*E*)-3-benzoyl-4-(2-phenylethenyl)pyrrole (**7j**, 3.0 g, 11.0 mmol) gave, after crystallization from Et_2O, **8j** as yellow crystals (1.7 g, 54%): mp 109−110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.64 (s, 3H), 6.88−6.97 (m, 3H), 7.19−7.33 (m, 3H), 7.43−7.54 (m, 5H), 7.72−7.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 37.0 (q), 120.4 (d), 121.5 (d), 121.5 (q), 124.8 (q), 126.0 (d), 126.7 (d), 127.1 (d), 127.9 (d), 128.3 (d), 128.7 (d), 130.7 (d), 131.1 (d), 137.9 (q), 140.5 (q), 191.4 (q); MS (relative intensity, %) *m*/*z* 77 (5.6), 105 (5.0), 167 (11.0), 182 (35.4), 210 (39.7), 258 (11.0), 287 (M^+, 100); HRMS *m*/*z* calcd for $C_{20}H_{17}NO$ 287.1310, found 287.1332. Anal. Calcd for $C_{20}H_{17}NO$: C, 83.60; H, 6.09; N, 4.90. Found: C, 83.52, H, 6.03, N, 4.82.

3-Benzoyl-1-(*tert*-butoxycarbonyl)-4-phenylpyrrole (9a). 3-Benzoyl-4-phenyl-pyrrole (**7a**, 6.4 g, 26 mmol), di-*tert*-butyl dicarbonate (6.2 g, 29 mmol), and *t*-BuOK (0.56 g, 5.0 mmol) in THF (200 mL) were refluxed for 1 h. The reaction mixture was poured into water (50 mL), and the solution was extracted with Et_2O (2 × 75 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. The crude product was filtered through a short column of basic Al_2O_3 (CH_2Cl_2). The eluent was concentrated to give **9a** as a pale yellow solid (7.0 g, 78%), pure according to ^{1}H NMR. Crystallization from EtOH (96%) gave **9a** as glassy crystals: mp 129−131 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.63 (s, 9H), 7.23−7.30 (m, 3H), 7.36−7.41 (m, 5H), 7.50−7.53 (m, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.84−7.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 27.8 (q), 85.2 (s), 119.1 (d), 124.8 (s), 126.6 (d), 126.9 (d), 128.0 (d), 128.1 (d), 128.4 (d), 128.8 (s), 129.5 (d), 132.3 (d), 133.3 (s), 138.6 (s), 148.0 (s), 191.1 (s); MS (relative intensity, %) *m*/*z* 28 (87.74), 32 (18.80), 39 (10.4), 41 (32.4), 44 (15.9), 57 (100), 77 (14.8), 115 (16.1), 170 (60.8), 246 (20.8), 247 (54.5), 291 (36.9), 347 (M^+, 7.3); HRMS *m*/*z* calcd for $C_{22}H_{21}NO_3$ 347.1521, found 347.1522. Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03. Found: C, 75.88, H, 6.11, N, 4.06.

3-Benzoyl-1-(*tert*-butoxycarbonyl)-4-(2-phenylethenyl)-pyrrole (9j). Following the procedure described for **9a**, (*E*)-3-benzoyl-4-(2-phenylethenyl)pyrrole (**7j**, 3.0 g, 11.0 mmol), di-*tert*-butyl dicarbonate (2.64 g, 12.1 mmol), and *t*-BuOK (0.22 g, 2.0 mmol) in THF (75 mL) gave, after crystallization from EtOH (96%), **9j** as off-white crystals (3.32 g, 81%), mp 130−132 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.63 (s, 9H), 6.98 (d, J = 16.6 Hz, 1H), 7.23−7.37 (m, 3H), 7.45−7.60 (m, 8H), 7.84−7.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 27.8 (q), 85.3 (s), 117.2 (d), 120.2 (d), 124.4 (s), 126.2 (s), 126.3 (d), 127.2 (d), 128.2 (d), 128.4 (d), 129.1 (d), 129.3 (d), 132.0 (d), 137.4 (s), 139.3 (s), 147.9 (s), 191.5 (s); MS (relative intensity, %) *m*/*z* 69 (79.8), 81 (46.2), 95 (14.6), 105 (15.5), 121 (10.1), 137 (18.6), 149 (11.2), 168 (31.5), 196 (33.0), 244 (9.3), 256 (8.9), 273 (100), 317 (46.8), 373 (M^+, 7.5); HRMS *m*/*z* calcd for $C_{24}H_{23}NO_3$ 373.1678, found 373.1678. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.99; H, 6.24; N, 3.78.

3-Benzoyl-1-methyl-2,4-diphenylpyrrole (10). 3-Benzoyl-1-methyl-4-phenyl-2-(trimethylstannyl)pyrrole (**5a**, 0.42 g, 1.0 mmol), bromobenzene (0.17 g, 1.1 mmol), and bis(triphenylphosphine)palladium(II) chloride (14 mg, 0.02 mmol) were refluxed in THF (5 mL) for 40 h. The reaction mixture was concentrated and filtered through a short column of basic Al_2O_3 (CH_2Cl_2). The crude product was purified by crystallization from EtOH (96%) to give **10** as pale yellow crystals (0.22 g, 65%): mp 120−122 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.60 (s, 3H), 6.86 (s, 1H), 7.07−7.31 (m, 13H), 7.64−7.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 34.7 (q), 121.0 (s), 121.1 (d), 125.8 (d), 125.9 (s), 127.4 (d), 127.9 (d), 127.9 (d), 128.1 (d), 129.7 (d), 130.5 (d), 130.9 (s), 131.7 (d), 134.6 (s), 137.3 (s), 138.8 (s), 193.7 (s); MS (relative intensity, %) *m*/*z* 77 (4.6), 169 (11.1), 217 (5.2), 260 (85.5), 337 (M^+, 100); HRMS *m*/*z* calcd for $C_{24}H_{19}NO$ 337.1467, found 337.1460. Anal. Calcd for $C_{24}H_{19}NO$: C, 85.42; H, 5.68; N, 4.15. Found: C, 85.31; H, 5.68; N, 4.13. Alternatively, 3-benzoyl-2,4-diphenylpyrrole[11] was methylated according to the procedure described for **8a**. The compound so obtained was identical with compound **10** according to ^{1}H NMR and ^{13}C NMR.

3-Benzoyl-1-(*tert*-butoxycarbonyl)-2,4-diphenylpyrrole (11). 3-Benzoyl-1-(*tert*-butoxycarbonyl)-4-phenyl-2-(trimethylstannyl)pyrrole (**6a**, 0.26 g, 0.5 mmol), bromobenzene (0.85 g, 0.55 mmol), and bis(triphenylphosphine)palladium(II) chloride (7.0 mg, 0.01 mmol) were refluxed in THF (5 mL) for 70 h. The reaction mixture was concentrated and filtered through a short column of basic Al_2O_3 (CH_2Cl_2). The crude product was purified by crystallization from 2-propanol to give **11** as a white solid (0.15 g, 71%): mp 92−93 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.31 (s, 9H), 7.13−7.31 (m, 13H), 7.55 (s, 1H), 7.64−7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 27.4 (q), 84.5 (s), 118.9 (d), 125.9 (s), 126.6 (s), 126.7 (d), 127.3 (d), 127.7 (d), 127.8 (d), 127.8 (d), 128.2 (d), 129.5 (d), 130.2 (d), 132.0 (s), 132.5 (d), 133.2 (s), 135.0 (s), 137.8 (s), 148.8 (s), 193.9 (s); MS (relative intensity, %) *m*/*z* 57 (44.8), 105 (14.3), 189 (6.6), 217 (7.7), 246 (54.5), 306 (5.2), 323 (100), 367 (42.4), 423 (M^+, 20.4); HRMS *m*/*z* calcd for $C_{28}H_{25}NO_3$ 423.1834, found 423.1834. Anal. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 78.74; H, 6.02; N, 3.31.

1,4-Di[3-benzoyl-1-methyl-4-phenyl-2-pyrrolyl]-benzene (12). Pyrrole **5a** (0.85 g, 2.0 mmol), 1,4-dibromobenzene (0.24 g, 1.0 mmol), and bis(triphenylphosphine)palladium(II) chloride (28 mg, 0.04 mmol) were refluxed in THF (10 mL) for 70 h. After cooling, the white precipated solid was collected and washed with pentane (25 mL) to give **12** (0.30 g, 50%), pure according to ^{1}H NMR. Crystallization from a mixture of EtOH (96%)−CH_2Cl_2 (1:1) gave **12** as white crystals, mp 295−296 °C: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.56 (s, 6H), 6.93 (s, 2H), 7.15−7.20 (m, 8H), 7.24−7.28 (m, 6H), 7.34−7.36 (m, 6H), 7.70 (d, J = 7.02 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 34.7 (q), 121.0 (s), 121.4 (d), 125.9 (d), 126.2 (s), 127.4 (d), 128.0 (d), 128.1 (d), 129.7 (d), 130.2 (d), 130.6 (s), 131.5 (d), 134.5 (s), 136.8 (s), 139.0 (s), 193.5 (s); MS (relative intensity, %) *m*/*z* 44 (7.3), 105 (24.4), 221 (5.4), 259 (5.1), 298 (5.4), 519 (8.1), 596 (M^+, 100); HRMS *m*/*z* calcd for $C_{42}H_{32}N_2O_2$ 596.2464, found 596.2509. Anal. Calcd for $C_{42}H_{32}N_2O_2$: C, 84.53; H, 5.41; N, 4.70. Found: C, 83.78; H, 5.40; N, 4.62.

1,4-Di[3-benzoyl-1-(*tert*-butoxycarbonyl)-4-phenyl-2-pyrrolyl]benzene (13). Pyrrole **6a** (0.51 g, 1.0 mmol), 1,4-dibromobenzene (0.12 g, 0.5 mmol), and tetrakis(triphenylphosphine)palladium(0) (23 mg, 0.02 mmol) were refluxed in toluene (10 mL) and aqueous Na_2CO_3 (1 M, 10 mL) for 138 h. After cooling, the reaction mixture was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. After column chromatography (basic Al_2O_3, CH_2Cl_2), the first fraction gave

13 as a pale yellow solid. Crystallization from EtOH (96%) gave **13** as pale yellow crystals (75 mg, 21%): the compound decomposed at ca. 190 °C;[18] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.13 (s, 18H), 7.13−7.26 (m, 20H), 7.51 (s, 2H), 7.60−7.62 (m, 4H); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 27.2 (q), 84.8 (s), 119.0 (d), 126.3 (s), 126.3 (s), 126.7 (d), 127.5 (d), 127.8 (d), 128.2 (d), 129.3 (d), 129.5 (d), 131.6 (s), 132.6 (d), 133.2 (s), 133.9 (s), 137.8 (s), 148.8 (s), 193.6 (s); MS and HRMS were not determined due to thermal instability of the compound.

3-Benzoyl-2-bromo-1-methyl-4-phenylpyrrole (14). A solution of pyrrole **5a** (2.54 g, 6.0 mmol) in THF (50 mL) was cooled to −70 °C. NBS (1.17 g, 6.6 mmol) was added in small portions; then stirring was continued for 30 min at −70 °C. Next, the reaction mixture was stirred at 0 °C for 25 h. Water (25 mL) was added, and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL), dried ($MgSO_4$), and filtered through a short column of basic Al_2O_3 (CH_2Cl_2). Concentration of the eluent gave **14** as a pale yellow oil. Crystallization from 2-propanol gave **14** as white crystals (1.78 g, 87%), pure according to ^{1}H NMR. **14**: mp 107−108 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.70 (s, 3H), 6.89 (s, 1H), 7.10−7.38 (m, 8H), 7.73−7.78 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 35.7 (q), 107.4 (s), 121.2 (d), 121.7 (s), 126.1 (d), 126.9 (s), 127.8 (d), 127.8 (d), 128.0 (d), 129.9 (d), 132.2 (d), 134.0 (s), 138.0 (s), 129.3 (s); MS (relative intensity, %) *m*/*z* 77 (14.8), 130 (23.1), 155 (12.4), 183 (29.4), 262 (82.7), 264 (81.6), 339 (M^+, 100); HRMS *m*/*z* calcd for $C_{18}H_{14}BrNO$ 339.0259, found 339.0261. Anal. Calcd for $C_{18}H_{14}BrNO$: C, 63.55; H, 4.15; N, 4.12; Br, 23.49. Found: C, 63.08; H, 4.12; N, 4.12; Br, 23.65.

3-Benzoyl-2-bromo-1-(*tert*-butoxycarbonyl)-4-phenylpyrrole (15). A solution of pyrrole **6a** (2.0 g, 4.0 mmol) in THF (25 mL) was cooled to −70 °C. NBS (0.76 g, 4.3 mmol) was added in small portions; then stirring was continued for 30 min at −70 °C. Next, the reaction mixture was stirred at 0 °C for 24 h. Na_2SO_3 (0.81 g, 6.5 mmol) was added, and the mixture was stirred for 15 min; then the solvent was removed. CCl_4 (20 mL) was added, the mixture was filtered, and the filtrate concentrated. The crude product was dissolved in CH_2Cl_2, washed with water (2 × 50 mL), dried ($MgSO_4$), and filtered through a short column of basic Al_2O_3 (CH_2Cl_2), and the eluent was removed to give **15** as a colorless oil (1.28 g, 75%), pure according to ^{1}H NMR. **15**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.66 (s, 9H), 7.16−7.56 (m, 9H), 7.84−7.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 27.8 (q), 85.9 (s), 102.3 (s), 120.2 (d), 127.1 (d), 127.4 (d), 127.5 (s), 127.6 (s), 128.0 (d), 128.3 (d), 128.3 (d), 130.0 (d), 132.5 (s), 133.2 (d), 137.1 (s), 147.5 (s), 192.5 (s); MS (relative intensity, %) *m*/*z* 57 (74.0), 77 (12.9), 105 (11.3), 123 (9.3), 140 (6.7), 169 (15.1), 189 (6.9), 217 (8.8), 248 (40.0), 325 (100), 369 (10.7), 425 (M^+, 9.7); HRMS *m*/*z* calcd for $C_{22}H_{20}BrNO_3$ 425.0611, found 425.0586.

4-Benzoyl-1-methyl-2,3-diphenylpyrrole (18). 4-Benzoyl-2,3-diphenylpyrrole[17] was methylated according to the procedure described for **8a**. **18**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.57 (s, 3H), 7.09 (br s, 5H), 7.19−7.46 (m, 9H), 7.81−7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 35.3 (q), 121.8 (s), 124.6 (s), 125.7 (d), 127.3 (d), 127.7 (d), 128.2 (d), 129.3 (d), 129.9 (d), 130.4 (d), 130.9 (d), 131.1 (s), 131.2 (d), 133.4 (s), 134.5 (s), 139.9 (s), 190.9 (s); MS (relative intensity, %) *m*/*z* 69 (5.8), 77 (4.9), 105 (11.7), 169 (8.9), 189 (5.5), 217 (8.5), 245 (5.4), 260 (59.5), 337 (M^+, 100); HRMS *m*/*z* calcd for $C_{24}H_{19}NO$ 337.1467, found 337.1452. Anal. Calcd for $C_{24}H_{19}NO$: C, 85.42; H, 5.68; N, 4.15, Found: C, 85.24; H, 5.60; N 4.16.

Supporting Information Available: ^{1}H and/or ^{13}C NMR spectra of compounds **3h**, **8a**, **13**, and **15** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) For thermolytic removal of the Boc group, see: Rawal, V. H.; Cava, M. P. *Tetrahedron Lett.* **1985**, *26*, 6141.