Unconventional Regiospecific Syntheses of Aromatic Carbonamides and Thiocarbonamides by Means of Tin-Mediated Friedel-Crafts Reactions†

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Friedel-Crafts reactions of stannylarenes **1** with tosyl isocyanate (TsNCO, **2**) give *N*-tosylcarbonamides **3** via ipso substitution of the stannyl group. Thus, unconventionally substituted aromatic carbonamides can be obtained. The combination of the reaction of **1** and **2** with that of **1** and chlorosulfonyl isocyanate (**14**) allows one-pot syntheses of *N*-(arylsulfonyl)-substituted aromatic carbonamides with optional substitution patterns on both aromatic rings. The known ipso-specific substitutions of stannylarenes with **14** are extended to bi- and tricyclic arenes as well as to thiophenes **6** and **22**. One stannyl group can serve as a leaving group for two aromatic systems, as shown with diaryldialkyltins **29**. Also, stannylalkanes such as **27** react with **14** to afford alkylsulfonyl isocyanates and products of further reactions, such as **28**. From the reactions of **1** with ethoxycarbonyl isothiocyanate (**32**), ortho- and meta-substituted aromatic thiocarbonamides **33** which are potential precursors for further syntheses, are accessible. The scope, limitations, and mechanism of these electrophilic substitutions are outlined.

Introduction

"Electrophilic aromatic substitution is one of the cornerstones of organic chemistry. No single field of organic chemistry has received so much attention as that of electrophilic substitution of benzene and its derivatives."[1] Nevertheless, the reaction, in many cases, still has considerable drawbacks:[1,2] (1) when a second or third substituent is introduced the regioselectivity is generally governed by the substituents already present, and unconventional positions are not accessible; (2) the yields are often not as high as desirable from ecological (production of chemical waste) and economical (the energy and time required for separation of byproducts) viewpoints; and (3) the use of weak electrophiles is often restricted or impossible.

More research is needed to overcome these drawbacks. In electrophilic aromatic substitutions, the most common leaving group is the proton.[1,2] Ipso substitution, which is known in the field of nucleophilic aromatic substitution,[2] is a strategy for obtaining unconventional substitution patterns in which the proton is replaced by a group that is split off more easily by the electrophile. The silyl group (R_3Si, usually R = Me) is used for this purpose.[3,4] Often, however, its effect is not strong enough to overcome the usual directing forces, and ipso substitution is not achieved.[4c]

Recently, organotin compounds have found an increasing number of applications as reagents in organic syntheses (for example, in Pd-catalyzed Stille reactions[5]) and in many other fields.[6] In a number of cases, for example, in proto- and halodestannylations, the R_3Sn aromatic substituent exhibits an even higher leaving ability than the R_3Si group.[1,7-9]

The reactions of aromatics with phenyl isocyanate PhNCO and $AlCl_3$[10] (sometimes under drastic conditions), which lead to aromatic carbonamides, have been described. The regioselectivity is conventional. However, using stannylated aromatics as starting materials, we have obtained ortho- and meta-substituted carbonamides in high yields with exclusive ipso substitution under mild conditions.[11] Here we describe, for the first time, reactions of stannylated aromatics with tosyl isocyanate (TsNCO, **2**) and ethoxycarbonyl isothiocyanate (**32**) and new reactions of these aromatics with chlorosulfonyl isocyanate (**14**). These reactions allow simple and regiospecific access to aromatic carbonamides and thiocarbonamides. The yields are, in general, high or even quantitative, and the conditions are surprisingly mild.

Results and Discussion

There is a need for uncomplicated and effective syntheses of unusually substituted aromatic carbonamides, which are becoming increasingly important for the preparation of molecules with biological activity.[12] The reaction

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‡ Deceased.

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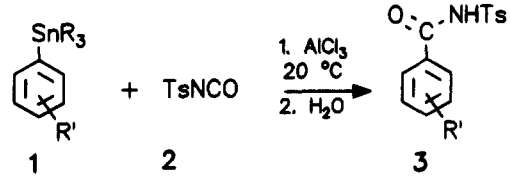
of arenes with 4-tolylsulfonyl isocyanate TsNCO (2)[13] is a convenient, simple method for the preparation of N-tosylated amides. Yet, as in most Friedel–Crafts reactions, only the para compounds are accessible, and a large excess of the aromatic starting material is essential.[13] The synthetic scope of this method is decidedly broadened by the use of a trialkylstannyl leaving group, which allows the synthesis of ortho- and meta-substituted amides **3e–h** at room temperature (eq 1) without an excess of aromatics 1.



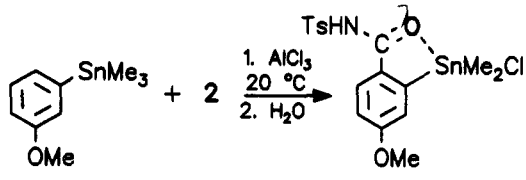
1 2 3 (1)

R, R': a) Bu, H b) Me, 4–Me c) Bu, 4–MeO
d) Bu, 4–Cl e) Bu, 2–Me f) Me, 3–Me
g) Bu, 2–MeO h) Me, 2–Cl

For example, substitution ortho to a methyl or a methoxy group can be achieved without any contamination by the para isomer, and the reaction also runs smoothly with deactivating chloro substituents. Moreover, only 1 equiv of $AlCl_3$ is necessary for satisfactory (and sometimes nearly quantitative) yields (83–98%), whereas 2 equiv are needed for nonstannylated aromatics.[13] For practical use, the Bu_3Sn substituent is recommended because of the much higher toxicity of the Me_3Sn derivatives.

For comparison with 1, we have prepared the corresponding *m*-methyl(trimethylsilyl)benzene. Under the same conditions used for 1, it still had not reacted with 2 after 2 days.

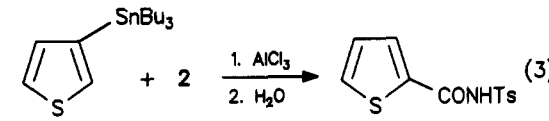
With a strongly directing substituent on the aromatic ring, however, the stannyl reactivity is overcome by that of the other substituent; the reaction of 3-(trimethylstannyl)anisol (4) with TsNCO (2) gives a para-substituted product, and subsequently a chlorodemethylation of the stannyl moiety gives 5 (eq 2). This para-substitution has



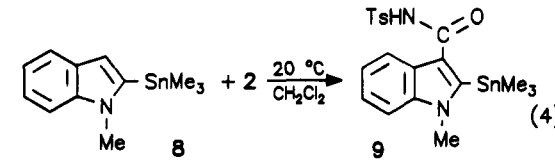
4 5 (2)

also been observed in the reactions of 4 with diazonium salts and with (chlorosulfonyl)amides.[14,15] The IR spectrum of amide 5 shows of a carbonyl absorption at 1621 cm^{-1}. The carbonyl absorptions of the corresponding ortho- and para-substituted compounds (**3c** and **g**) appear at about 1700 cm^{-1}. The shift is due to complexation of the tin atom of 5 with the carbonyl group.

With heteroaromatic stannanes 6 and 8, the 2- and 3-carboxylated isomers, 7 and 9, respectively, are formed (eqs 3 and 4). No catalysts is needed for the formation of 9. In contrast to the reaction of 4, 6, and 8 with 2 (eqs 2–4), in which the stannyl moiety does not determine the



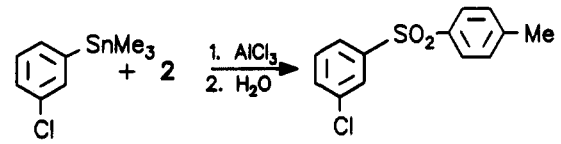
6 7 (3)



8 9 (4)

site of the electrophilic attack, the reactions of 4, 6, and 8 with phenyl isocyanate yield ipso substitution of the R_3Sn group.[11,16] The lack of ipso substitution in the reactions of 2 is probably due to the electron withdrawing effect of the sulfonyl group in 2. This effect decreases the availability of the N electron pair for interaction with the tin atom[11] and thus results in only a small amount of ipso substitution (see the discussion of the mechanism below).

Surprisingly, if chloro-3-(trimethylstannyl)benzene (**10**) is stirred with TsNCO (2) under conditions that in the other cases lead to the formation of the corresponding amides (eq 1), sulfone **11** is obtained (eq 5). The



10 11 (5)

deactivation of the meta position of **10** by the chloro substituent seems to lower the overall reactivity too much for a reaction with the original electrophile (**12**) (the Hammett constants for Cl are $\sigma^+_m = +0.40$, $\sigma^+_p = +0.115$[17]).

$$TolSO_2N{=}C^+O^-AlCl_3 \rightleftharpoons TolSO_2^{+-}NCOAlCl_3$$

12 13

Apparently, more reactive species **13**, which is in equilibrium[13] with **12** to a small extent, can—at least within the unusually long reaction time needed here—compete, and sulfodestannylation results.

Chlorosulfonyl isocyanate (CSI, **14**) reacts with (trialkylaryl)stannanes 1, without any catalyst, to afford the corresponding arylsulfonyl isocyanates **15** at room temperature.[18] In all cases, we obtained exclusive ipso substitution, even with strongly directing or deactivating substituents on the aromatic ring.[18] (With (trimethylsilyl)benzene and its *m*-methyl derivative, no reaction occurs under the same conditions.) Bond formation between the aryl system and **14** takes place not at the electrophilic center of the latter, the isocyanato group,[19] but at the chloro–sulfur bond. Reactions of crude arylsulfonyl isocyanates **15** with water, amines, or alcohols lead to the corresponding derivatives.[18]

The isocyanato group in **15** allows simple and effective one-pot syntheses. For example, usually substituted sulfilimines **16** or formamidines **17** are obtained when we apply dimethyl sulfoxide or dimethylformamide (eq 6). Presumably the intermediate [2 + 2] cycloadducts shown in eq 6 split off CO_2 spontaneously at room temperature.

(13) (a) Mc Farland, J. W.; Yao, L. C. *J. Org. Chem.* **1970**, *35*, 123. (b) Seefelder, M. *Chem. Ber.* **1963**, *96*, 3243. (c) Effenberger, F.; Gleiter, R.; Heider, L.; Niess, R. *Chem. Ber.* **1968**, *101*, 502.
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(15) Wicenec, C.; Neumann, W. P. *Chem. Ber.* **1993**, *126*, 763.
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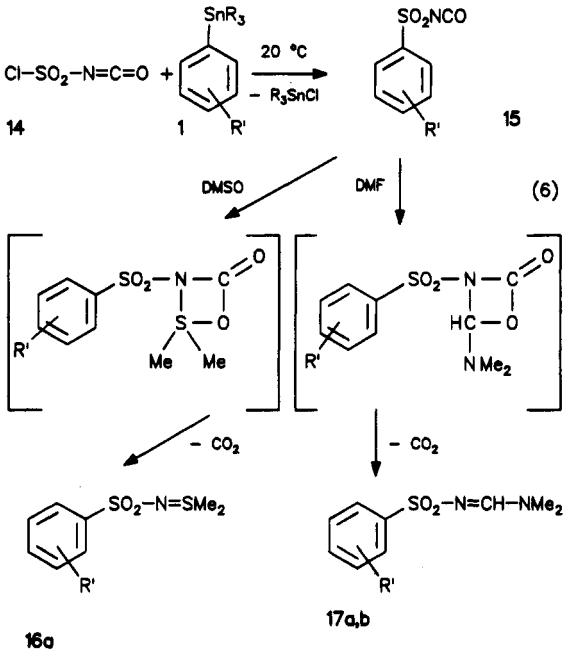
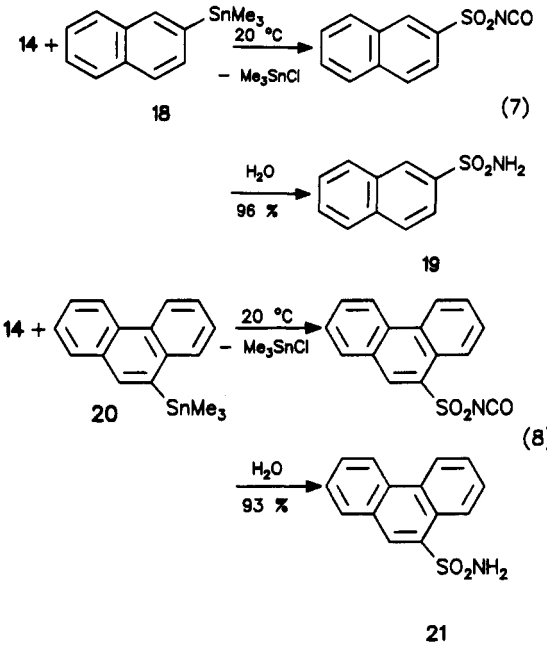


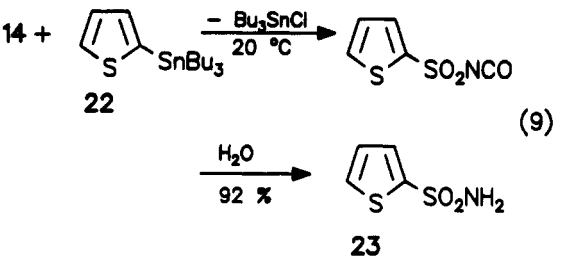
16a

	a	b
2, R	Me	Me
2, 4 5 , R'	4-Me	3-Cl

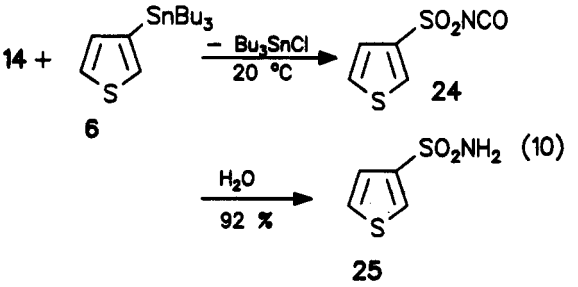
The ipso-specific introduction of the sulfonyl isocyanato group into other aromatics, for example, naphthalene and phenanthrene, can also be achieved via **14** (eqs 7 and 8).



The corresponding silanes (e.g., (trimethylsilyl)benzene, 3-(trimethylsilyl)toluene) and the nonstannylated aromatics do not react under these conditions. Usually the latter require the presence of aluminum trichloride for sufficient reactivity,[19] and there are relatively few examples of nonstannylated heterocyclic arenes that undergo electrophilic substitutions with **14** without a Lewis acid.[20] One of the few is thiophene, which is converted into the corresponding thiophene-2-carbamide by reaction with **14** and subsequent hydrolysis.[20b] Compound **14** usually attacks thiophene at the activated 2-position with its electrophilic isocyanato group. In contrast, the corresponding stannane affords the sulfonyl isocyanate (eq 9).

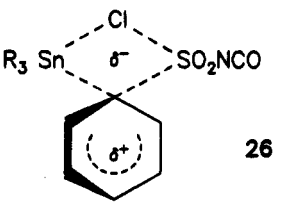


The stannyl leaving group causes the electrophile to attack with inverted chemoselectivity. The same reaction occurs when the R_3Sn group occupies the usually less activated 3-position of thiophene (eq 10). The regio- and



chemoselectivity are now completely determined by the stannyl group. The reason for this must be an interaction of the stannyl group with the attacking electrophile as early as on the way to the transition state.

A cationic intermediate[21] suggested in several earlier investigations for some other cases is, in the present cases, only an insufficient approximation to the transition state for electrophilic reactions of (trialkyaryl)stannanes. Instead, a one-step process involving the formation of a cyclic, four-membered transition state with direct interaction of the electrophile and the stannyl group was proposed.[22] The reactions of stannyl-substituted aromatics with **14**, especially the ipso-specific formation of compounds **23** and **25** from stannanes **6** and **22**, leads us to the assumption that a four-membered transition state such as **26** is responsible for the observed chemoselectivity of electrophile **14**.



26

This transition state allows for intramolecular nucleophilic assistance (which was found to be operative in

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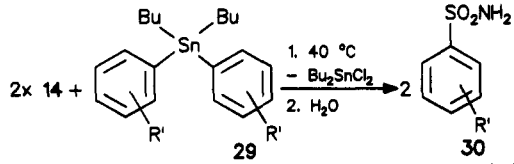
protodestannylations[23]) and for the formation of the trialkyltin chloride, the most stable of the final organotin products possible here. This interpretation is supported by the fact that tetraalkylstannanes with linear alkyl groups, such as **27**, which are unlikely to form cationic intermediates[1] react with CSI **14** to afford the corresponding alkylsulfonyl isocyanates and, by means of further reactions, products like **28** (eq 11). Tetra-*n*-octyltin reacts similarly but much more slowly. In any case, only one C–Sn bond is split.

$$14 + \underset{\mathbf{27}}{BuSnBu_3} \xrightarrow[-Bu_3SnCl]{20\ ^\circ C} BuSO_2NCO \xrightarrow[56\%]{H_2O} \underset{\mathbf{28}}{BuSO_2NH_2} \quad (11)$$

The efficiency of the reaction of **14** and stannylarenes **1** can be increased by linking two aryl rings with one stannyl leaving group. For example, (dibutyldiaryl)stannanes **29** react at 40 °C with **14** to afford the corresponding arylsulfonyl isocyanates and, after hydrolysis, arylsulfonamides (eq 12). Both rings can be substituted with a



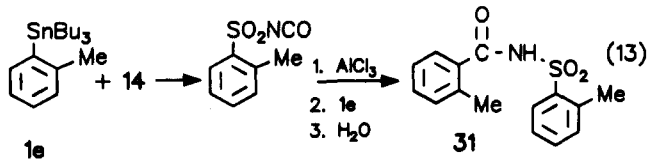
(12)

	a	b	c	d
29, 30, R'	H	2-Me	3-Me	4-Me

2-, 3-, or 4-Me group, and only ipso-substituted products **30** are formed. (The yields of 47–94% in the 10 mmol scale experiments refer to the stoichiometric equation.) Thus, only 0.5 mol of the organotin is required for the substitution of 1.0 mol of the aromatic system. Moreover, the byproduct to be separated is not R_3SnX but R_2SnX_2, which can easily be converted into insoluble $(R_2SnO)_n$, e.g., $(Bu_2SnO)_n$.

The presence of three or four phenyl rings on one tin atom lowers the reactivity. The reaction of **14** with butyltriphenylstannane affords, even under drastic conditions (13 h at 40 °C or 92 h at 100 °C), only a maximum yield of 32% of the stoichiometric amount of phenylsulfonamide, and from the reaction of tetraphenylstannane, only 7% of the stoichiometric amount of phenylsulfonamide was obtained after 73 h at 100 °C.

The synthetic value of the reactions shown in eqs 1 and 6 can be extended by combining them. Thus, stirring 1 equiv of a stannane **1** with 1 equiv of **14** at room temperature (eq 6) and subsequent addition of 1 equiv of $AlCl_3$ and another equivalent of a stannane **1** (eq 1) yield substituted amides such as **31** (eq 13).

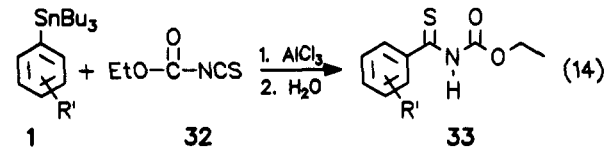


(13)

(23) (a) Berwin, H. J. *J. Chem. Soc., Chem. Commun.* **1972**, 237. (b) Traylor, T. G.; Hanstein, W.; Berwin, H. J. *J. Am. Chem. Soc.* **1970**, *92*, 7476.

The increasing interest in the use of thiocarbonamides for technical and synthetic purposes[24,25] caused us to search for alternatives to the existing methods for their preparation.[26,27] We successfully extended the common Friedel–Crafts reaction to stannanes, but we were unable to obtain N-substituted aromatic thioamides from the reactions of equimolar amounts of (trialkylaryl)stannanes **1** and PhNCS, Me_2NCSCl, or PhCONCS.

With the reactions of stannylarenes **1** with ethoxycarbonyl isothiocyanate (**32**), however, we were able to extend the Papadopoulos method[28] to the synthesis of ortho- and meta-substituted *N*-(ethoxycarbonyl)thiocarbamides **33**. Equation 14 presents a selection of typical examples, which should encourage broader application of this valuable method.



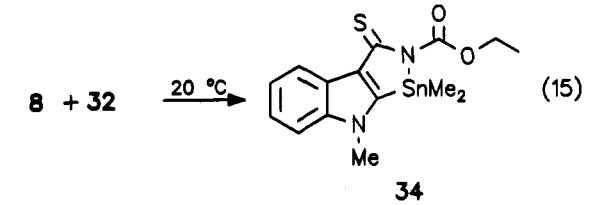
(14)

R' =	2-Me	3-Me	4-Me	2-Cl	3-Cl	4-Cl
1 =	**1e**	**1i**	**1j**	**1k**	**1l**	**1d**
33 =	**33a**	**33b**	**33c**	**33d**	**33e**	**33f**

In this reaction (eq 14), the tributylstannyl derivatives of **1** are superior to the corresponding (trimethylstannyl)-arenes. During workup, amides **33a–f** are separated from the byproducts by extraction with aqueous NaOH. In this step, tributyltin chloride (which is formed as a byproduct) can easily be removed by washing with diethyl ether, whereas the water-soluble trimethyltin chloride has to be removed by additional purification procedures, which are, in general, not very effective.

Amides **33** are versatile starting materials for a large number of syntheses,[29–32] and the use of the stannyl leaving group yields isomers of these interesting compounds that, to our knowledge, have hitherto been unaccessible.

The reaction of **32** with 1-methyl-2-(trimethylstannyl)indole (**8**) leads to the formation of the heretofore unknown tricycle **34** (eq 15). This multifunctional molecule might well be useful as a building block for further syntheses.



(15)

The electrophile attacks the activated 3-position of the indole nucleus, and subsequent interaction of the intro-

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(25) (a) Barton, D. H. R. *Tetrahedron* **1992**, *47*, 2529. (b) Metzner, P. *Synthesis* **1992**, 1185.
(26) Schöberl, A.; Wagner, A. In *Houben-Weyl*; Thieme: Stuttgart, 1955; Vol. 9.
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(28) Papadopoulos, E. P. *J. Org. Chem.* **1976**, *41*, 962.
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duced functional group and the trimethylstannyl moiety causes the loss of one methyl group. This nonipso substitution can be regarded, in analogy to what has been said in the case of phenyl isocyanate and tosyl isocyanate (2), as a result of the electron-withdrawing effects of the ethoxycarbonyl group.

Conclusion

Because the use of trialkylstannyl-substituted aromatics in Friedel–Crafts reactions allows—within the stated limits given by our basic examples—the regioselective introduction of interesting functional groups with unusual isomer patterns, it is possible to envisage the application of this method for the synthesis of a broad variety of natural products and biomolecules. This will be a part of our future work.

Experimental Section

General. NMR spectra were recorded at 60 MHz (^{1}H, Me_4Si as external standard), 75.47 MHz (^{13}C, $CDCl_3$ as internal standard), and 111.92 MHz (^{119}Sn, Me_4Sn as internal standard) in acetone-d_6, unless otherwise stated. Chemical shifts δ are given in ppm. IR spectra were taken in KBr. The absorption frequencies are given in cm^{-1}. Mass spectra were taken at 70 eV [*m/z* (relative intensity)]. Melting points are uncorrected.

Stannylarenes **1**, **4**, and **10** were prepared from the corresponding Grignard reagents.[8,11,14,15,18] Stannanes **6**, **8**, and **22**[33] were prepared from the corresponding lithium reagents.

3-(Tributylstannyl)thiophene (6). BuLi (0.039 mol) in 40 mL of hexane and 25 mL of diethyl ether was cooled to −78 °C. 3-Bromothiophene (5.79 g, 0.035 mol) was added over a period of 15 min. The mixture was stirred for 15 min, and then 11.4 g (0.0350 mol) tributyltin chloride was added over a period of 15 min. The mixture was allowed to warm to rt, the solvents were removed at 10 °C/15 Torr, and the residue was distilled: 11.20 g (86%); bp 130 °C/0.01 Torr.

1-Methyl-2-(trimethylstannyl)indole (8). According to the procedure given in ref 33, from 13.1 g (0.001 mol) of 1-methylindole, 0.101 mol of BuLi in hexane, and 20.0 g (0.998 mol) of trimethyltin chloride was obtained 21.2 g (72%) of **8**: bp 101 °C/10^{-3} Torr; ^{1}H NMR (CCl_4) δ 0.25 (s, 9 H, $SnMe_3$, $^2J_{SnH}$ = 54 Hz), 3.28 (s, 3 H, CH_3), 6.30–7.63 (m, 5 H, Ar H); ^{13}C NMR δ −8.8 (CH_3), 33.68 (CH_3), 108.76, 111.09, 118.73, 119.84, 121.09 (CH), 128.81, 139.51, 141.95 (Cq); MS 295 (58) [M$^+$], 280 (100), 250 (60), 144 (34), 130 (42), 117 (72). Anal. Calcd for $C_{12}H_{19}NSn$: C, 49.0; H, 5.8; N, 4.8. Found: C, 49.0; H, 6.0; N, 4.8.

Dialkyldiarylstannanes **29** were prepared from the corresponding Grignard reagents.[34]

Dibutylbis(2-methylphenyl)stannane (29b). Prepared from 2-bromotoluene, Mg, and Bu_2SnCl_2: ^{1}H NMR ($CDCl_3$) δ 1.24–2.05 (m, 18 H, Bu), 2.71 (s, 6 H, CH_3), 7.40–7.95 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 11.19, 27.25, 29.08 (CH_2), 13.57, 24.99 (CH_3), 125.15, 128.56, 129.02, 136.68 (CH), 140.92, 144.48 (Cq); ^{119}Sn NMR ($CDCl_3$) δ −67.7 ($^1J_{SnC}$ = 439 Hz); MS 359 (84), 303 (64), 211 (64), 120 (31), 91 (58). Anal. Calcd for $C_{22}H_{32}Sn$: C, 63.66; H, 7.71. Found: C, 63.0; H, 8.0.

Dibutylbis(3-methylphenyl)stannane (29c). Prepared from 3-bromotoluene, Mg, and Bu_2SnCl_2: ^{1}H NMR ($CDCl_3$) δ 1.40–2.23 (m, 18 H, Bu), 2.82 (s, 6 H, CH_3), 7.58–7.90 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 10.21, 27.35, 28.98 (CH_2), 13.61, 21.43 (CH_3), 127.95, 129.12, 133.71, 137.29 (CH), 137.26, 140.07 (Cq); ^{119}Sn NMR ($CDCl_3$) δ −71.7 ($^1J_{SnC}$ = 439 Hz); MS 325 (48), 268 (80), 211 (86), 182 (100), 120 (52), 91 (54). Anal. Calcd for $C_{22}H_{32}Sn$: C, 63.66; H, 7.71. Found: C, 62.8; H, 7.8.

Ethoxycarbonyl isothiocyanate (**32**) was prepared according to the published procedure.[31] The other starting compounds are commercially available. All reactions were carried out under argon, and solvents were dried according to standard procedures prior to use.

General Procedure for the Reaction of Stannylarenes 1a–h with Tosyl Isocyanate (2). Compound **2** (10.0 mmol) was added to 10.0 mmol of $AlCl_3$ in 20 mL of CH_2Cl_2 over a period of 5 min. The mixture was stirred for 10 min, and then 10.0 mmol of **1** was added within 10 min. This mixture was stirred for 15 h (for 48 h for **3d** and **3h**) at rt and was then poured on 50 g of ice and 50 mL of diluted hydrochloric acid. The aqueous phase was extracted twice with 30 mL of CH_2Cl_2. The combined organic layers were washed twice with 20 mL of diluted hydrochloric acid and then dried with magnesium sulfate. The solvent was removed under reduced pressure, and the residue was stirred with pentane and, if necessary, recrystallized from an appropriate solvent. Following this procedure, amides **3a–h** were obtained as colorless solids.

***N*-[(4-Methylphenyl)sulfonyl]benzenecarboxamide (3a).** From 3.67 g (10.0 mmol) of **1a**: yield 2.53 g (92%); mp 147 °C (heptane) (lit.[35] mp 147 °C); IR 3315, 1710, 1452.

***N*-[(4-Methylphenyl)sulfonyl]-4-methylbenzenecarboxamide (3b).** From 2.55 g (10.0 mmol) of **1b**: yield 2.40 g (83%); mp 136 °C (benzene/heptane (1/1)) (lit.[13a] mp 137–138 °C); IR 3300, 1699, 1612, 1429, 1405.

***N*-[(4-Methylphenyl)sulfonyl]-4-methoxybenzenecarboxamide (3c).** From 3.97 g (10.0 mmol) of **1c**: yield 2.99 g (98%); mp 174 °C (ethanol) (lit.[13a] mp 176–177 °C); IR 3220, 1669, 1608, 1440.

***N*-[(4-Methylphenyl)sulfonyl]-4-chlorobenzenecarboxamide (3d).** From 4.01 g (10.0 mmol) of **1d**: yield 2.75 g (89%); mp 193 °C (benzene) (lit.[13a] mp 192–194 °C); IR 3225, 1700, 1595, 1440.

***N*-[(4-Methylphenyl)sulfonyl]-2-methylbenzenecarboxamide (3e).** From 3.81 g (10.0 mmol) of **1e**: yield 2.54 g (88%); mp 112 °C (heptane/toluene (1/1)) (lit.[35] mp 112.5–113 °C); ^{1}H NMR δ 1.63 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3), 6.40–7.47 (m, 8 H, Ar H), 10.10 (s, 1 H, NH); IR 3265, 1714, 1598, 1442, 1416.

***N*-[(4-Methylphenyl)sulfonyl]-3-methylbenzenecarboxamide (3f).** From 2.55 g (10.0 mmol) of **1f**: yield 2.66 g (92%); mp 133 °C (hexane) (lit.[35] mp 132–132.5 °C); ^{1}H NMR δ 1.97 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 6.83–7.73 (m, 8 H, Ar H), 10.40 (s, 1 H, NH); IR 3300, 1699, 1457, 1439.

***N*-[(4-Methylphenyl)sulfonyl]-2-methoxybenzenecarboxamide (3g).** From 3.97 g (10.0 mmol) of **1g**: yield 2.80 g (92%); mp 131 °C (heptane/toluene (1/4)); ^{1}H NMR δ 1.87 (s, 3 H, CH_3), 3.57 (s, 3 H, OCH_3), 6.37–7.80 (m, 8 H, Ar H) 10.00 (s, 1 H, NH); ^{13}C NMR δ 22.18, 57.67 (CH_3), 113.77, 122.66, 129.89, 130.82, 132.91, 136.31 (CH), 121.10, 128.30, 146.13, 159.46, 163.91 (Cq); IR 3275, 1686, 1601, 1487, 1470, 1466.

***N*-[(4-Methylphenyl)sulfonyl]-2-chlorobenzenecarboxamide (3h).** From 2.67 g (10.0 mmol) of **1h**: yield 2.63 g (85%); mp 106 °C (benzene); ^{1}H NMR δ 1.90 (s, 3 H, CH_3), 6.50–7.63 (m, 8 H, Ar H), 10.23 (s, 1 H, NH); ^{13}C NMR δ 21.47 (CH_3), 127.91, 129.08, 129.38, 130.13, (CH), 131.75, 132.07, 138.07, 145.96, 165.26, (Cq); IR 3255, 1702, 1598, 1443. MS 245 (10), 155 (31), 139 (32), 108 (71), 107 (32), 91 (100). Anal. Calcd. for $C_{14}H_{12}ClNO_3S$: C, 54.3; H, 3.9; N, 4.5. Found: C, 54.6; H, 3.9; N, 4.6.

***N*-[(4-Methylphenyl)sulfonyl]-2-(chlorodimethylstannyl)-4-methoxybenzenecarboxamide (5).** According to the procedure for the preparation of **3a–h**, from 2.71 g (10.0 mmol) of **4** was obtained 4.00 g (82%) of **5**: mp 209 °C dec (CH_2Cl_2); ^{1}H NMR δ 0.00 (s, 6 H, $^2J_{SnH}$ = 72 Hz, $SnMe_2$), 1.87 (s,3 H, CH_3), 3.37 (s, 3 H, OCH_3), 6.38–8.10 (m, 7 H, Ar H), 10.80 (s, 1 H, NH); ^{13}C NMR δ 0.18, 21.51, 56.11, (CH_3), 115.72, 122.90, 129.49, 130.30, 130.80 (CH), 125.92, 136.90, 146.19, 151.21, 165.51, 170.28 (Cq); ^{119}Sn NMR δ −27.8, $^1J_{SnC}$ = 556 Hz. IR 3200, 1621, 1588, 1554, 1527, 1518, 1490; MS 438 (10) [M$^+$ − HCl − Me],389 (56), 282 (100), 36 (68). Anal. Calcd for $C_{17}H_{20}ClNO_4SSn$: C, 41.8; H, 4.1; N, 2.9. Found: C, 41.6; H, 4.1; N, 2.8.

***N*-[(4-Methylphenyl)sulfonyl]-2-thiophenecarboxamide (7).** Following the procedure for the preparation of **3a–h**, from 3.73 g (10.0 mmol) of **6** was obtained 2.70 g (96%) of **7**: mp

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179 °C (heptane) (lit.[36] mp 180–182 °C); IR 3275, 1688, 1597, 1525, 1430, 1406.

***N*-[(4-Methylphenyl)sulfonyl]-1-methyl-2-(trimethylstannyl)indole-3-carboxamide (9).** Compound 8 (2.95 g, 10.0 mmol) was added to 1.97 g (10.0 mmol) of 2 in 20 mL of CH_2Cl_2 over a period of 20 min. The mixture was stirred for 17 h at rt, and then the solvent was removed under reduced pressure. The residue was stirred with pentane for 30 min, filtered off, and dried: yield 4.23 g (86%) of 9; mp 176 °C; ^{1}H NMR δ −0.30 (s, 9 H, $SnMe_3$; $^2J_{SnH}$ = 57 Hz), 1.90 (s, 3 H, CH_3), 3.37 (s, 3 H, CH_3), 6.40–7.70 (m, 8 H, Ar H); ^{13}C NMR δ −5.15 (SnMe, $^1J_{SnC}$ = 375 Hz), 21.90, 35.67 (CH_3), 122.40, 123.55, 129.30, 129.80, 130.10, 130.45 (CH), 139.24, 141.33, 142.17, 143.80, 145.34, 156.56, 165.27 (Cq); ^{119}Sn NMR δ −47.8. IR 3270, 1667, 1626, 1599, 1474, 1424, 1400, 1366, 1338; MS 447 (6) [M$^+$ − Me], 328 (30), 165 (100), 158 (100), 130 (25), 91 (30). Anal. Calcd. for $C_{20}H_{24}N_2O_3SSn$: C, 48.9; H, 4.9; N, 5.7. Found: C, 49.1; H, 4.9; N, 5.8.

1-Chloro-3-[(4-methylphenyl)sulfonyl]benzene (11). Compound 10 (2.75 g, 10.0 mmol), 1.97 g (10.0 mmol) of 2, and 1.33 g (10.0 mmol) of $AlCl_3$ in 20 mL of CH_2Cl_2 were stirred for 172 h. After workup as described for **3a–h**, 2.19 g (82%) of 11 was obtained: mp 125 °C (ethanol/water (3/2)) (lit.[37] mp 127 °C); ^{1}H NMR δ 2.00 (s, 3 H, CH_3), 6.73–2.60 (m, 8 H, Ar H); IR 1597, 1322, 1294, 1159; MS 266 (55) [M$^+$], 139 (66), 107 (100), 91 (53).

***N*-[(4-Methylphenyl)sulfonyl]dimethylsulfilimine (16a).** 4-(Trimethylstannyl)toluene (**1b**) (2.55 g, 10.0 mmol) and 1.41 g (10.0 mmol) of 14 in 10 mL of CH_2Cl_2 were stirred for 10 h at rt. Then 3.12 g (40.0 mmol) of DMSO was added over a period of 30 min. The mixture was stirred for 10 h, the solvent was removed at 10 °C/15 Torr, and the residue was recrystallized from ethanol/water (1/1): yield 1.90 g (82%) of **16a**; mp 156 °C (lit.[38] mp 157–158 °C); ^{1}H NMR δ 1.83 (s, 3 H, CH_3), 2.15 (s, 6 H, SMe_2), 6.58–7.25 (m, 4 H, Ar H).

***N*,*N*-Dimethyl-*N'*-[(4-methylphenyl)sulfonyl]formamidine (17a).** 4-(Trimethylstannyl)toluene (**1b**) (2.55 g, 10.0 mmol) and 2.41 g (10.0 mmol) 14 were stirred in 10 mL of CH_2Cl_2 for 10 h. Then 2.92 g (40 mmol) of DMF was added within 30 min. The mixture was stirred for 10 h, and the solvent was removed at 20 °C/15 Torr. The residue was recrystallized from ethanol/water (1/1): yield 1.81 g (80%) **17a**; mp 134 °C (lit.[30] mp 133–134 °C); IR 1628, 1432, 1348; ^{1}H NMR δ 1.93 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 2.70 (s, 3 H, CH_3), 6.70–7.23 (m, 4 H, Ar H), 7.65 (s, 1 H, CH).

***N*,*N*-Dimethyl-*N'*-[(3-chlorophenyl)sulfonyl]formamidine (17b).** According to the procedure described for **17a**, from 1.41 g (10.0 mmol) of 14, 2.76 g (10.0 mmol) of chloro-3-(trimethylstannyl)benzene (**10**), and 2.92 g (40.0 mmol) DMF was obtained 1.77 g (72%) of **17b**: mp 118 °C; ^{1}H NMR δ 2.45 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 6.92–7.37 (m, 4 H, Ar H), 7.65 (s, 1 H, CH); ^{13}C NMR δ 35.46 (CH_3), 125.53, 126.80, 131.38, 132.17, 160.86 (CH), 134.78, 146.56 (Cq); IR 3075, 2935, 1633, 1579. MS 246 (25) [M$^+$], 111 (47), 71 (100), 44 (100). Anal. Calcd for $C_9H_{11}ClN_2O_2S$: C, 43.82; H, 4.46; N, 11.36. Found: C, 43.9; H, 4.3; N, 11.3.

Naphthalene-2-sulfonamide (19). Following the procedure for the preparation of sulfonamides given in ref 18, from 2.90 g (10.0 mmol) of 2-(trimethylstannyl)naphthalene (**18**) and 2.12 g (15.0 mmol) of 14 was obtained 1.96 g (96%) of **19**: mp 212 °C (ethanol) (lit.[39] mp 217 °C); IR 3340, 3250, 1687, 1622, 1587.

Phenanthrene-9-sulfonamide (21). Following the procedure for the preparation of sulfonamides given in ref 19, from 3.41 g (10.0 mmol) of 9-(trimethylstannyl)phenanthrene (**20**) and 2.12 g (15.0. mmol) of 14 was obtained 2.40 g (93%) of **21**: mp 192–193 °C (ethanol) (lit.[40] mp 193.5 °C): ^{1}H NMR δ 6.38 (s, 2 H, NH_2), 7.00–8.60 (m, 9 H, Ar H); IR 3335, 3235, 1493, 14449, 1307, 1136.

Thiophene-2-sulfonamide (23). Following the procedure for the preparation of **21**, from 3.73 g (10.0 mmol) of 2-(tributylstannyl)thiophene (**22**) and 1.41 g (10.0 mmol) of 14 was obtained 1.50 g (92%) of **23**: mp 146 °C (ethanol) (lit.[41] mp 146–147 °C); IR 3355, 3265, 3100, 1532; MS 163 (100) [M$^+$], 147 (88), 99 (58), 83 (11).

Thiophene-3-sulfonamide (25). Following the procedure for the preparation of **21**, from 3.73 g (10.0 mmol) of 3-(tributylstannyl)thiophene (**6**) and 1.41 g (10.0 mmol) of 14 was obtained 0.90 g (65%) of **25**: mp 155 °C (water) (lit.[42] mp 155–157 °C); IR 3360, 3265, 3110, 1535; MS 163 (64) [M$^+$], 147 (68), 99 (66), 83 (24).

***n*-Butylsulfonamide (28).** Following the procedure for the preparation of **21**, from 3.47 g (10.0 mmol) of tetrabutyltin **27** and 2.12 g (15.0 mmol) of 14 was obtained 0.77 g (56%) of **28**: mp 45 °C (pentane) (lit.[43] mp 47.5–49 °C). The yield is not increased by using excess 14: ^{1}H NMR ($CDCl_3$) δ 0.88–2.30 (m, 7 H), 3.25 (t, 2 H, CH_2), 5.00 (s, 2 H, NH_2); IR 3355, 3270, 2970, 2880, 1557, 1467. Likewise, tetra-*n*-octyltin gives, at 80 °C after 20 h, a 10% yield (isolated) of *n*-octylsulfonamide, mp 70 °C.

Arenesulfonamides 30a–d. Arene sulfonamides **30a–d** were prepared according to the procedure for the arene sulfonamides given in ref 18 from 5.00 mmol of dibutyldiarylstannanes **29a–d** and 2.12 g (15.0 mmol) of 14. The reactions were carried out for 10 h at 40 °C. The sulfonamides were characterized by their melting points and their IR and NMR data (see ref 18). In each case, only the ipso-substituted isomer was found.

Phenylsulfonamide (30a). From dibutyldiphenylstannane (**29a**): yield 1.37 g (87%).

2-Methylbenzenesulfonamide (30b). From dibutylbis(2-methylphenyl)stannane (**29b**): yield 1.44 g (84%).

3-Methylbenzenesulfonamide (30c). From dibutylbis(3-methylphenyl)stannane (**29c**): yield 0.80 g (47%) when the reaction was carried out at 40 °C in CH_2Cl_2; yield 0.84 g (49%) when the reaction was carried out for 23 h at 100 °C in chlorobenzene.

4-Methylbenzenesulfonamide (30d). From dibutylbis(4-methylphenyl)stannane (**29d**): yield 1.61 g (94%).

***N*-[(2-Methylphenyl)sulfonyl]-2-methylbenzenecarboxamide (31).** Compound **1e** (3.81 g, 10.0 mmol) and 1.41 g (10.0 mmol) of 14 were stirred in 20 mL of CH_2Cl_2 for 15 h at rt. Then, 1.33 g (10.0 mmol) of $AlCl_3$ was added, and the mixture was stirred for 20 min. After the dissolution of $AlCl_3$, 3.81 g (10.0 mmol) of **1e** was added. The mixture was stirred at rt for 15 h, and after workup as described for the preparation of **3a–h**, 2.08 g (72%) of **31** was obtained: mp 138 °C (CH_2Cl_2/heptane (1/1)); ^{1}H NMR δ 2.00 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 6.90–8.07 (m, 8 H, Ar H), 10.60 (s, 1 H, NH); ^{13}C NMR δ 19.64, 20.28 (CH_3), 126.41, 126.87, 128.26, 131.79, 131.87, 133.12, 134.25, 134.38 (CH), 137.50, 138.34, 138.64, 167.67 (Cq); IR 3265, 1713, 1491, 1475, 1457. MS 289 (11) [M$^+$], 225 (11), 135 (15), 119 (83), 108 (100), 91 (62). Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.3; H, 5.2; N, 4.8. Found: C, 62.1; H, 5.2; N, 4.7.

General **Procedure for the Preparation of the Thioamides 33.** Compound **32** (1.31 g, 10.0 mmol) was added at 0 °C to 2.66 g (20.0 mmol) of $AlCl_3$ in 20 mL of CH_2Cl_2, and the mixture was stirred for 5 min. Stannane 1 (10.0 mmol) in 5 mol of CH_2Cl_2 was added over a period of 10 min. The mixture was stirred for 2 h at 0 °C and for 2 h at rt and then poured on 50 mL of ice-cooled diluted hydrochloric acid. This mixture was stirred for 20 min and then extracted three times with 20 mL of CH_2Cl_2. The combined layers were extracted with four 40-mL portions of 10% aqueous NaOH. These combined aqueous layers were washed twice with 50 mL of diethyl ether and then acidified at 0 °C with concentrated hydrochloric acid to pH 2. The resulting aqueous solution was extracted three times with 20 mL of CH_2Cl_2, and the organic layer was dried with magnesium sulfate. Then the solvent was removed under reduced pressure. The residue was a pale yellow oil that crystallized in the cases of the para-substituted compounds. Amides **33** were obtained in sufficient purity (NMR, elemental analysis) and consisted of only the ipso isomer. The thioamides turned from pale yellow to dark orange after standing for more than 1 day.

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***N*-(Ethoxycarbonyl)-2-methylbenzenethiocarboxamide (33a).** From 3.81 g (10.0 mmol) of **1e**: yield 1.85 g (83%); oil; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.3 Hz, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 3.92 (q, J = 7.3 Hz, 2 H, CH_2), 6.77–7.20 (m, 4 H, Ar H), 9.72 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.28, 18.53 (CH_3), 62.10 (CH_2), 124.68, 125.62, 128.22, 129.1 (CH), 131.51, 142.21, 149.00, 207.22 (Cq). IR 3245, 2990, 1766, 1601, 1496; MS 223 (48) [M$^+$], 194 (65), 150 (61), 134 (100), 118 (46), 117 (58), 116 (67). Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.2; H, 5.8; N, 6.3. Found: C, 59.6; H, 5.8; N, 6.0.

***N*-(Ethoxycarbonyl)-3-methylbenzenethiocarboxamide (33b).** From 3.81 g (10.0 mmol) of **1i**: yield 1.67 g (75%); oil; ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7.3 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.10 (q, J = 7.3 Hz, 2 H, CH_2), 6.90–7.73 (m, 4 H, Ar H), 9.60 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.60, 20.66 (CH_3), 62.04 (CH_2), 123.69, 127.35, 127.49, 131.92 (CH), 137.29, 141.43, 150.68, 202.66, (Cq); IR 3255, 2990, 1751, 1605, 1587, 1510, 1412; MS 223 (89) [M$^+$], 179 (20), 135 (40), 91 (50). Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.2; H, 5.8; N, 6.3. Found: C, 59.3; H, 5.6; N, 6.6.

***N*-(Ethoxycarbonyl)-4-methylbenzenethiocarboxamide (33c).** From 3.81 g (10.0 mmol) of **1j**: yield 1.98 g (89%); mp 97 °C (lit.[28] mp 98–100 °C); IR 3190, 2990, 2915, 1751, 1714, 1687, 1607.

***N*-(Ethoxycarbonyl)-2-chlorobenzenethiocarboxamide (33d).** From 4.01 g (10.0 mmol) of **1k**: yield 1.27 g (52%); oil; ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.3 Hz, 3 H, CH_3), 4.00 (q, J = 7.3 Hz, 2 H, CH_2), 7.00–7.43 (m, 4 H, Ar H), 10.00 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.32 (CH_3), 60.40 (CH_2), 125.91, 128.13, 129.46 (CH), 127.34, 140.77, 148.98, 202.74 (Cq); IR 3220, 2990, 1765, 1665, 1655, 1637, 1618, 1591; MS 243 (82) [M$^+$], 208 (50), 180 (43), 155 (43), 138 (100), 102 (65). Anal. Calcd for $C_{10}H_{10}ClNO_2S$: C, 49.3; H, 4.1; N, 5.8. Found: C, 49.1; H, 4.0; N, 6.1.

***N*-(Ethoxycarbonyl)-3-chlorobenzenethiocarboxamide (33e).** From 4.0 g (10.0 mmol) of **1l**: yield 1.49 g (61%); oil; ^{1}H NMR ($CDCl_3$) δ 1.50 (t, J = 7.3 Hz, 3 H, CH_3), 4.30 (q, J = 7.3 Hz, 2 H, CH_2), 7.10–7.67 (m, 4 H, Ar H), 9.58 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 14.15 (CH_3), 62.98 (CH_2), 125.24, 127.41, 129.29, 131.27 (CH), 134.04, 143.30, 150.85, 201.72, (Cq); IR 3245, 2990, 2940, 1753, 1508, 1502; MS 243 (85) [M$^+$], 199 (25), 171 (25), 155 (67), 140 (64), 139 (71), 138 (100), 111 (65). Anal. Calcd for $C_{10}H_{10}ClNO_2S$: C, 49.3; H, 4.1; N, 5.8. Found: C, 48.5; H, 4.0; N, 6.1.

***N*-(Ethoxycarbonyl)-4-chlorobenzenethiocarboxamide (33f).** From 4.01 g (10.0 mmol) of **1d**: yield 1.51 g (62%); mp 119 °C (lit[28] mp 117–118 °C); IR 3185, 2980, 1758, 1718, 1682, 1592.

***N*-Methylindolo[2,3-*d*]-1,1-dimethyl-2-(ethoxycarbonyl)-1-stanna-2-azacyclopenten-4-thion-3 (34) by Reaction of 1-Methyl-2-(trimethylstannyl)indole (8) with 32.** Compound **8** (2.94 g, 10.0 mmol) and 1.31 g (10.0 mmol) of **32** were stirred in 15 mL CH_2Cl_2 for 24 h at rt. Then the solvent was removed under reduced pressure, the residue was stirred with 15 mL of pentane for 4 h and then recrystallized from pentane/CH_2Cl_2 (4/1): yield 2.51 g (62%) of **34**; pale yellow crystals; mp 150 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 6 H, $SnMe_2$, $^2J_{SnH}$ = 63 Hz), 1.50 (t, J = 7.3 Hz, 3 H, CH_3), 3.93 (s, 3 H, CH_3), 4.50 (q, J = 7.3 Hz, 2 H, CH_2), 7.11–7.53, 8.30–8.60 (m, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ –2.75 (CH_3, $^1J_{SnC}$ = 404 Hz), 14.40, 35.42 (CH_3), 62.19 (CH_2), 109.36, 121.57, 121.67, 123.27 (CH), 125.47, 127.95, 142.77, 155.12, 162.80, 165.96 (Cq); ^{119}Sn NMR ($CDCl_3$) δ 47.0. IR 3050, 2985, 2935, 1667, 1568, 1463, 1421, 1376, 1346, 1330; MS 410 (78) [M$^+$], 365 (32), 335 (26), 323 (45), 307 (92), 156 (100), 146 (33), 114 (32). Anal. Calcd for $C_{15}H_{18}N_2O_2SSn$: C, 44.5; H, 4.4; N, 6.9. Found: C, 44.5; H, 4.3; N, 6.5.

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