reaction has been performed in THF, exactly as previously described.[3] Along with 4-((dimethylamino)carbonyl)tetradecachlorotriphenylmethyl radical (Me_2NCO-PTM•), green solid (10.5% yield) has been obtained which has been characterized as in (b).

(b) A solution of radical ClCO-PTM• (0.28 g) in THF (75 mL) was saturated with Me_2N at room temperature and let stand for 52 h. I_2 (0.065 g) was added, and it was left undisturbed for 45 min. The resulting mass was worked up as in the reaction with radical PTM•. However, $CHCl_3$ was used as the eluent, giving a solid (0.26 g), which was recrystallized from hexane/$CHCl_3$ yielding 4-(dimethylamino)-4′-(dimethylcarbamoyl)tridecachlorotriphenylmethyl radical ($(Me_2N)(Me_2NCO)$>PTM•; 0.23 g, 80.5%), deep green solid, mp 253–255 °C; UV–vis (C_6H_{12}) (Figure 1) 220, 293 (sh), 383, 427 (sh), 590 (sh), 645 nm (ε 80 000, 8300, 21 000, 7700, 2350, 3400); IR (KBr) 2960, 2930, 2910–2850, 2795, 1666, 1523, 1460, 1443, 1403, 1348, 1323, 1266, 1236, 1203, 1196–1168, 1098, 1058, 968, 940, 803, 778, 738, 718, 693, 650, 623, 608, 585, 533, 458 cm^{-1}; ESR data, Table I. Anal. Calcd for $C_{24}H_{12}N_2OCl_{13}$: C, 35.8; H, 1.5; N, 3.5. Found: C, 36.9; H, 1.8; N, 4.2.

Acknowledgment. We wish to acknowledge our deep appreciation to the Centre d'Investigació i Desenvolupament (Consejo Superior de Investigaciones Científicas) for some laboratory facilities provided to them. Thanks are due to Mrs. A. Díez for the ESR spectra and to Mr. J. Vidal for the drawings. I.P. wishes to express her gratitude to the Ministerio de Educación y Ciencia of Spain for an extension to her F.P.I. fellowship.

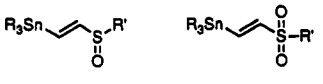
Palladium-Catalyzed Synthesis of Some New Olefinic Stannanes

Vittorio Farina* and Sheila I. Hauck

Bristol-Myers Squibb Research Institute, 5 Research Pkwy., P.O. Box 5100 Wallingford, Connecticut 06492-7660

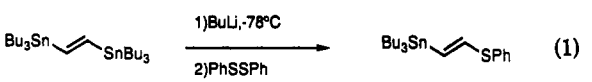
Received November 27, 1990

In connection with a medicinal chemistry project, we required a practical and general approach to a series of β-(trialkylstannyl)vinyl sulfoxides and sulfones exemplified by structures **1** and **2**. Olefinic stannanes have become very important synthetic intermediates, in the light of their versatile chemistry,[1] which has been recently expanded to include a variety of palladium-catalyzed coupling reactions.[2]



1 **2**

We initially examined a literature procedure,[3] describing the preparation of sulfones of the type represented by **2** from *trans*-1,2-bis(tributylstannyl)ethylene, **3**. It is reported that selective monolithiation of **3**, followed by quenching with phenyl disulfide, produced sulfide **4** in excellent yield. Oxidation then yielded the corresponding sulfone (eq 1).



(1)

3 **4**

In our hands, however, only poor yields of **4** could be obtained under a variety of experimental protocols (direct or inverse addition of the disulfide, temperatures as low as −100 °C). Control experiments established that monolithiation was a clean process (quenching with aldehydes produced allylic alcohols in almost quantitative yield), suggesting that the problematic step is the sulfenylation. Under our best conditions, 28–32% yields of **4** were obtained. We also found that aryl disulfides bearing electron-withdrawing groups on the ring failed completely to deliver the desired products. Both **5a** and **5b**, which are key compounds for our studies, could not be obtained at all by this protocol.

(2)

3

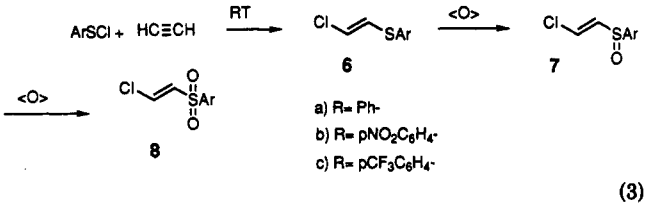
4 R=Ph, 28-32%

5a R=pNO$_2$-C$_6$H$_4$, 0%

5b R=pCF$_3$-C$_6$H$_4$, 0%

Due to the unsatisfactory results obtained, it was decided to investigate alternative approaches.

A potential route to **1** and **2** is suggested by the insertion reaction of acetylene with sulfenyl halides.[4] The procedure proved high-yielding and easy to scale up. Stepwise oxidation with *m*-chloroperbenzoic acid then provided sulfoxides **7** and sulfones **8** (eq 3).



(3)

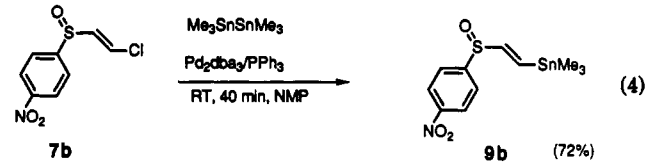
6 **7** **8**

a) R= Ph-

b) R= pNO$_2$C$_6$H$_4$-

c) R= pCF$_3$C$_6$H$_4$-

The only step left was now the introduction of the trialkylstannyl moiety. Unfortunately our preliminary attempts with Bu_3SnLi[5] and Bu_3SnCu,[6] using **7b** as a substrate, gave no reaction. We discovered, however, that when **7b** in *N*-methylpyrrolidinone (NMP) was treated with hexamethylditin and a catalytic amount of a homogeneous palladium catalyst at room temperature, the corresponding trimethylstannane was obtained in good yield (eq 4). The reaction was extended without problems to other sulfoxides and sulfones (see Table I).



(4)

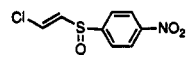
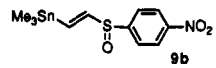
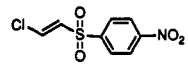
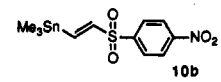
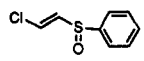
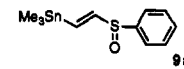
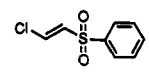
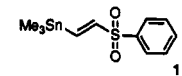
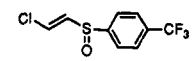
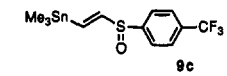
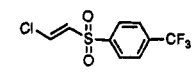
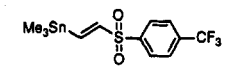
7b **9b** (72%)

Several observations need to be made. The palladium catalyst employed was tris(dibenzylideneacetone)bispalladium with added triphenylphosphine, but other

(1) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.
(2) Review: Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. In particular, see: Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.
(3) Keck, G. E.; Byers, J. H.; Tafesh, A. M. *J. Org. Chem.* **1988**, *53*, 1127.
(4) Montanari, F. *Gazz. Chim. Ital.* **1956**, *86*, 406.
(5) Ochiai, M.; Ukita, T.; Fujita, E. *Tetrahedron Lett.* *24*, 4025.
(6) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4264. Piers, E.; Chong, J. M. *J. Org. Chem.* **1982**, *47*, 1604. Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *65*, 78. For conjugate additions of silyl cuprates to unsaturated sulfoxides, see: Takaki, K.; Maeda, T.; Ishikawa, M. *J. Org. Chem.* **1989**, *54*, 58. For a study on higher order trialkyltin cuprates (which we did not try) see: Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065.

0022-3263/91/1956-4317$02.50/0

Table I. Palladium-Catalyzed Synthesis of Olefinic Stannanes from the Corresponding Chlorides

entry	substrate	product	conditions	% yield
1		 **9b**	rt, 40 min	72
2		 **10b**	rt, 85 min	47
3		 **9a**	rt, 4 h	78
4		 **10a**	rt, 90 min	60
5		 **9c**	rt, 4 h	84
6		 **10c**	rt, 4 h	81

common catalysts, such as palladium acetate plus phosphine, or $Pd(PPh_3)_4$, could be used. No reaction took place without palladium, with or without phosphines. There was very little ligand effect in this reaction: for example tri-2-furylphosphine, the ligand of choice in the coupling of vinyltins with electrophiles,[7] led to product formation at approximately the same rate as triphenylphosphine. Excess ligand did not appreciably slow down the reaction rate, in contrast with the coupling of vinyltins.[8]

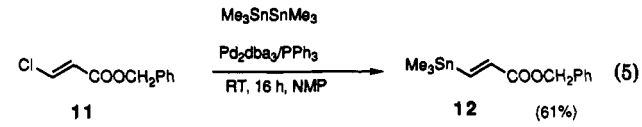
Oxygen or BHT (up to 0.5 equiv) had no effect on the rate, while water slightly enhanced the rate (10 equiv roughly doubled the rate for the conversion of **8b** to **9b**). As a consequence, the NMP used for the coupling need not be especially dry. Less polar solvents (such as THF) led to some reaction only at elevated temperatures, affording low yields of the products. The products appear to be somewhat unstable under the reaction conditions, and it is therefore important to monitor each reaction to completion. Unnecessarily long reaction times led to poorer yields.

Finally, no reaction was observed when the above procedure was modified by using hexabutylditin or hexamethyldisilane instead of hexamethylditin.

Hexaalkylditins have been used in palladium-catalyzed approaches to arylstannanes,[9] allylstannanes,[10] and α-diketones.[11] More recently, Wulff has extended this reaction to include vinyl triflates.[12] Vinylic chlorides, on the other hand, are seldom employed as partners in palladium-catalyzed couplings, probably due to the slow oxidative addition of Pd(0) with these substrates.

Indeed, oxidative addition of Pd(0) is documented for *activated* vinyl chlorides[13] only. Given the activated nature of our substrates, we feel that our results can be explained by the classical mechanism[1] involving oxidative addition, transmetalation, and reductive elimination, although other possibilities exist.[14]

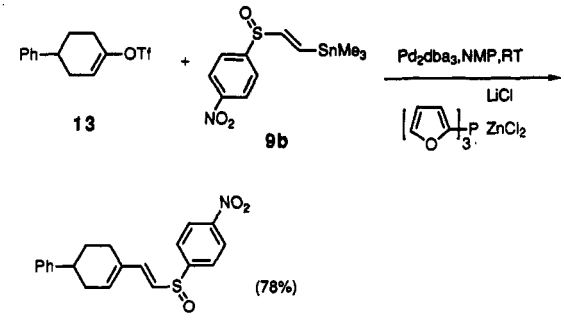
We briefly investigated extension of this chemistry to other activated chlorides. A β-chloroacrylate (**11**) nicely coupled under our standard conditions to yield stannane **12** (eq 5).



11 **12** (61%) (5)

Stannylacrylates like **12**, however, are also accessible by cuprate methodology.[15] Surprisingly, 3-chlorocyclohex-2-en-1-one did not participate in the above coupling under our conditions.

To illustrate the use of our synthons, stannane **9b** was submitted to a Stille coupling with vinyl triflate **12** under our modified conditions[7] to produce functionalized diene **14** (as a mixture of diastereomers) in good yield (eq 6). Sulfoxide-containing dienes are synthetically useful as diene partners in the inverse demand Diels–Alder reaction, in conjunction with the [2,3] sigmatropic shift of the resulting allylic sulfoxides.[16]



13 **9b** (6)

14

In conclusion, an efficient new route to olefinic stannanes bearing the sulfonyl and sulfinyl functions was developed. Coupling of these synthons with vinyl triflates provides a potentially general approach to dienyl sulfoxides and sulfones. Application of these compounds in medicinal chemistry will be discussed in due course.

(7) Farina, V.; Baker, S. R.; Benigni, D. A.; Hauck, S. I.; Sapino, C. *J. Org. Chem.* **1990**, *55*, 5833.
(8) Farina, V.; Krishnan, B. Manuscript in preparation.
(9) Azarian, D.; Dua, S. S.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C55. Bumagin, N. A.; Bumagina, I. G. *Dokl. Acad. Nauk SSSR* **1984**, *274*, 1103. Bumagin, N. A.; Gulevich, Yu. V.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim., No. 5* **1983**, 1137.
(10) Bumagin, N. A.; Kasatkin, A. N.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim., No. 3* **1984**, 636.
(11) Verlhac, J. B.; Chanson, E.; Jousseaume, B.; Quintard, J. P. *Tetrahedron Lett.* **1985**, *26*, 6075.
(12) Wulff, W. D.; Peterson, G. A.; Bauta, W. A.; Chan, K. S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 279.
(13) Fitton, P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 4. Onishi, M.; Yamamoto, H.; Hiraki, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1856.
(14) For example, oxidative addition of ditin derivatives to Pd(0) is probably involved in the palladium-catalyzed addition of hexamethylditin to 1-alkynes. See: Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45.
(15) Seitz, D. E.; Lee, S. H. *Tetrahedron Lett.* **1981**, *22*, 4909.
(16) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

Experimental Section

General experimental protocols are as previously described.[7] HPLC monitoring was carried out with a Phenomenex C-18 column (300 × 3.9 mm), eluting with 60% acetonitrile and 40% water (1.5 mL/min).

Reaction of Sulfenyl Chlorides with Acetylene. Sulfides **6a** and **6b** were prepared essentially as described by Montanari.[4] Sulfide **6c** was prepared as follows: *p*-(Trifluoromethyl)phenyl disulfide[17] (3.260 g, 9.200 mmol) in dry dichloromethane (40 mL) was treated with sulfuryl chloride[18] (0.80 mL, 9.958 mmol), and the solution was refluxed for 100 h, after which time additional sulfuryl chloride (0.80 mL) was added and the solution was refluxed overnight. NMR analysis indicated complete conversion of the disulfide to the corresponding sulfenyl chloride. Evaporation of the solvent in vacuo gave a crude product that was immediately dissolved in dry methyl acetate (30 mL), cooled at 0 °C, and treated with a stream of acetylene gas for 30 min. The container of red solution was then stoppered tightly, the bath was removed, and the mixture was stirred at room temperature for 4 d. Concentration of the pale yellow solution under vacuum, followed by flash chromatography of the residue (hexane), gave a colorless oil, 2.650 g (60% overall): ^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2 H) 7.37 (d, J = 8.2 Hz, 2 H), 6.54 (d, J = 10 Hz, 1 H), 6.50 (d, J = 10 Hz, 1 H). Anal. Calcd for $C_8H_6ClF_3S$: C, 45.29; H, 2.53; S, 13.43; Cl, 14.86. Found: C, 45.40; H, 2.56; S, 13.07; Cl, 14.52.

Preparation of β-Chlorovinyl Sulfoxides and Sulfones. Sulfide **6a** (2.360 g, 9.540 mmol) in dichloromethane (70 mL) at −25 °C was treated with 60% *m*-chloroperbenzoic acid (4.740 g, 16.50 mmol) in portions. After 30 min the mixture was filtered, and the filtrate was washed with 5% sodium bicarbonate, water, and brine. Chromatography of the residue on silica gel (5–10% EtOAc in hexane) gave sulfoxide **7a** (1.210 g, 42%), followed by sulfone **8a** (1.302 g, 49%).

7a: ^{1}H NMR ($CDCl_3$) δ 7.59–7.43 (m, 5 H), 6.95 (d, J = 13.2 Hz, 1 H), 6.59 (d, J = 13.2 Hz, 1 H); white solid, mp 35–8 °C (lit.[21] bp 132–3 °C (3 mm Hg)); HRMS calcd for C_8H_8SOCl (M+H) 186.9984, found 186.9985. Anal. Calcd for C_8H_7SOCl: C, 51.48; H, 3.78. Found: C, 51.59; H, 3.52.

8a: ^{1}H NMR ($CDCl_3$) δ 7.85–7.55 (m, 5 H), 7.36 (d, J = 13.1 Hz, 1 H), 6.68 (d, J = 13.1 Hz, 1 H); white solid, mp 49–50°C (lit.[4] mp 49–50 °C). Anal. Calcd for $C_8H_7SO_2Cl$: C, 47.41; H, 3.48. Found: C, 47.45; H, 3.32.

The following compounds were obtained in an analogous fashion.

7b: ^{1}H NMR ($CDCl_3$) δ 8.34 (d, J = 8.7 Hz, 2 H), 7.75 (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 13.2 Hz, 1 H), 6.63 (d, J = 13.2 Hz, 1 H); white solid, mp 83–4 °C (lit.[21] mp 83–4 °C); HRMS calcd for $C_8H_8ClNO_3S$ 231.9835, found 231.9828.

8b: ^{1}H NMR ($CDCl_3$) δ 8.42 (d, J = 9 Hz, 2 H), 8.09 (d, J = 9 Hz, 2 H), 7.58 (d, J = 13.1 Hz, 1 H), 6.76 (d, J = 13.1 Hz, 1 H); white solid, mp 154–56 °C (lit.[4] mp 158 °C).

7c: ^{1}H NMR ($CDCl_3$) δ 7.82–7.73 (m, 4 H), 7.06 (d, J = 13.2 Hz, 1 H), 6.70 (d, J = 13.2 Hz, 1 H); white solid, mp 57–58.5 °C; HRMS calcd for $C_9H_6ClF_3OS$ 254.9858, found 254.9857. Anal. Calcd for $C_9H_6ClF_3OS$: C, 42.45; H, 2.37. Found: C, 42.40; H, 2.35.

8c: ^{1}H NMR ($CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 2 H), 7.84 (d, J = 8.1 Hz, 2 H), 7.53 (d, J = 13 Hz, 1 H), 6.75 (d, J = 13 Hz, 1 H); white solid, mp 130–2 °C; HRMS calcd for $(C_9H_6ClF_3)_2S$ 270.9807, found 270.9803. Anal. Calcd for $C_9H_6ClF_3O_2S$: C, 39.94; H, 2.23. Found: C, 40.13; H, 2.25.

Palladium-Catalyzed Stannylation of β-Chlorovinyl Sulfoxides and Sulfones. Preparation of 9b: Sulfoxide **7b** (119.5 mg, 0.5158 mmol) was dissolved in dry NMP (5 mL), and triphenylphosphine (10.8 mg, 0.0412 mmol) and tris(dibenzylideneacetone)bispalladium (4.7 mg, 0.0051 mmol) were added. The yellow solution was degassed with argon, and hexamethylditin (380 mg, 1.160 mmol) was added by syringe. The mixture turned bright red within 5–10 min and was worked up after 30 min by addition of water and ethyl acetate. The organics were washed with water (3×) and dried over sodium sulfate. Evaporation and chromatography of the residue (20–30% EtOAc in hexane) gave **9b** as a yellow powder; 135 mg (72%): mp 77–8 °C; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, J = 8.7 Hz, 2 H), 7.76 (d, J = 8.7 Hz, 2 H), 7.45 (d, J = 17.9 Hz, 1 H), 6.59 (d, J = 17.9 Hz, 1 H), 0.22 (s, 9 H); HRMS calcd for $C_{11}H_{16}NO_3S^{116}Sn$ (M + H) 357.9872, found 357.9870. Anal. Calcd for $C_{11}H_{15}NO_3SSn$: C, 36.70; H, 4.20; N, 3.89. Found: C, 36.74; H, 4.10; N, 3.81.

The following compounds were prepared in similar fashion (reaction times and yields are given in Table I).

10b: ^{1}H NMR ($CDCl_3$) δ 8.32 (d, J = 9 Hz, 2 H), 8.00 (d, J = 9 Hz, 2 H), 7.83 (d, J = 18.2 Hz, 1 H), 6.60 (d, J = 18.2 Hz, 1 H), 0.20 (s, 9 H); HRMS calcd for $C_{11}H_{16}NO_4S^{116}Sn$ (M + H) 373.9821, found 373.9820. Anal. Calcd for $C_{11}H_{15}NO_4SSn$: C, 35.14; H, 4.02; N, 3.72. Found: C, 35.35; H, 3.96; N, 3.64.

9a: ^{1}H NMR ($CDCl_3$) δ 7.58–7.40 (m, 5 H), 7.36 (d, J = 18 Hz, 1 H), 6.57 (d, J = 18 Hz, 1 H), 0.21 (s, 9 H); yellow oil; HRMS calcd for $C_{11}H_{17}OS^{116}Sn$ (M + H) 313.0021, found 313.0016. Anal. Calcd for $C_{11}H_{16}OSSn$: C, 41.98; H, 4.82. Found: C, 41.94; H, 5.12.

10a: ^{1}H NMR ($CDCl_3$) δ 7.89–7.49 (m, 5 H), 6.64 (d, J = 18.4 Hz, 1 H), 0.22 (s, 9 H); yellow solid, mp 52–4 °C; HRMS calcd for $C_{11}H_{17}O_2S^{116}Sn$ (M + H) 328.9970, found 328.9967. Anal. Calcd for $C_{11}H_{16}O_2SSn$: C, 39.92; H, 4.87. Found: C, 40.16; H, 4.97.

9c: ^{1}H NMR ($CDCl_3$) δ 7.77–7.69 (m, 4 H), 7.42 (d, J = 17.9 Hz, 1 H), 6.58 (d, J = 17.9 Hz, 1 H), 0.20 (s, 9 H); colorless oil; HRMS calcd for $C_{12}H_{16}F_3OS^{116}Sn$ (M + H) 380.9895, found 380.9889. Anal. Calcd for $C_{12}H_{15}F_3OSSn$: C, 37.63; H, 3.95; S, 8.37; Sn, 30.99. Found: C, 37.68; H, 3.98; S, 8.19; Sn, 31.07.

10c: ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 8 Hz, 2 H), 7.83 (d, J = 8 Hz, 2 H), 7.82 (d, J = 18.2 Hz, 1 H), 6.66 (d, J = 18.2 Hz, 1 H), 0.25 (s, 9 H); white solid, mp 81–3 °C; judged homogeneous by TLC (silica gel, ethyl acetate/hexane) and ^{1}H NMR (>95% pure); HRMS calcd for $C_{12}H_{16}F_3O_2S^{116}Sn$ (M + H) 396.9844, found 396.9828.

(*E*)-Benzyl 2-(Trimethylstannyl)acrylate (12). (*E*)-Benzyl 2-chloroacrylate (154.8 mg, 0.783 mmol) was dissolved in dry NMP (2 mL), and triphenylphosphine (16.4 mg, 0.062 mmol) was added, followed by tris(dibenzylideneacetone)bispalladium (7.2 mg, 0.0079 mmol) under argon. After 5 min hexamethylditin (322 mg, 0.983 mmol) was added and the solution was stirred at room temperature overnight. Workup as for **9b** and chromatography (5% EtOAc in hexane) gave **12** as an oil, 155.9 mg (61%): ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J = 19.5 Hz, 1 H), 7.36–7.23 (m, 5 H), 6.33 (d, J = 19.5 Hz, 1 H), 0.17 (s, 9 H); HRMS calcd for $C_{13}H_{19}O_2{}^{116}Sn$ (M + H) 323.0406, found 323.0401. Anal. Calcd for $C_{13}H_{18}O_2Sn$: C, 47.90; H, 5.56. Found: C, 48.21; H, 5.67.

Palladium-Catalyzed Coupling of 9b. 1-(Triflyloxy)-4-phenylcyclohexane[19] (131.6 mg, 0.430 mmol) was dissolved in dry NMP (5 mL) and tri-3-furylphosphine[20] (3.9 mg, 0.0178 mmol) was added, followed by anhydrous lithium chloride (54.6 mg, 1.288 mmol), zinc chloride (118 mg, 0.866 mmol), and tris(dibenzylideneacetone)bispalladium (3.9 mg, 0.0042 mmol). The solution was degassed, stirred at room temperature for 2 h, diluted with EtOAc, and washed with water 4 times. Drying was followed by filtration and evaporation, and the crude product was chromatographed with 20–40% EtOAc in hexane to yield a colorless foam of **14** (as a mixture of 2 isomers at sulfur), 119 mg (78%), judged homogeneous by TLC and NMR (>95% pure by ^{1}H NMR spectroscopy): ^{1}H NMR ($CDCl_3$) δ 8.37 (two overlapping d, J = ca. 9 Hz, 2 H overall), 7.82 (two overlapping d, J = ca.9 Hz, 2 H overall), 7.31–7.20 (m, 5 H), 7.12 (d, J = 15.3 Hz, 1 H), 6.31 (br s, 1 H), 6.22 (d, J = 15.3 Hz, 1 H), 2.81 (m, 1 H), 2.65–2.15 (m, 4 H), 2.02 (m, 1 H), 1.78 (m, 1 H); HRMS calcd for $C_{20}H_{20}NO_3S$ (M + H) 354.1164, found 354.1161. Anal. Calcd for $C_{20}H_{19}NO_3S$: C, 67.96; H, 5.42; N, 3.96. Found: C, 66.67; H, 5.20; N, 3.83.

Acknowledgment. We are grateful to Dr. S. E. Klohr and Ms. S. E. Hill for the accurate mass determinations.

Supplementary Material Available: Proton NMR spectra of compounds **10c** and **14** (2 pages). Ordering information is given on any current masthead page.

(17) Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 2100.
(18) Harpp, D. N.; Mathiaparanam, P. *J. Org. Chem.* **1972**, *37*, 1367.
(19) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.
(20) Allen, D. W.; Hutley, B. G.; Mellor, R. T. J. *J. Chem. Soc., Perkin Trans. 2* **1972**, 63.
(21) Montanari, F.; Negrini, A. *Gazz. Chim. Ital.* **1959**, *89*, 1543.