O_4·10H_2O was added and the solution was stirred for several hours. The organic layer was decanted, the solvent was evaporated, and the residue was purified by preparative thin-layer chromatography on silica gel (hexane/EtOAc (5:1)) to give **17a** (11.3 mg): IR ($CHCl_3$) 3600, 2920, 1460, 1020 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.21–2.04 (m, 4 H), 2.06–2.36 (m, 3 H), 2.56 and 3.11 (ABq, J = 15.6 Hz, 2 H), 3.32 and 3.62 (ABq, J = 11.0 Hz, 2 H), 6.06 (t, J = 3.7 Hz, 1 H), 7.09–7.36 (m, 4 H); MS m/z 200 (M^+), 182 ($M^+ - H_2O$), 169 ($M^+ - CH_2OH$), 141, 128, 115, 91; HR-MS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1184.

Palladium Cross-Coupling Reactions of Aryl Fluorosulfonates: An Alternative to Triflate Chemistry

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A new and efficient electrophilic partner for palladium(0)-catalyzed cross coupling is reported. Aryl fluorosulfonates are readily prepared in high yield by treatment of the appropriate phenol with fluorosulfonate anhydride. The palladium-catalyzed coupling reactions of these fluorosulfonates with vinyl- and aryltin reagents, as well as organozinc chlorides, takes place under mild conditions in a regio- and stereoselective manner.

A variety of preparative methods have evolved that utilize substituted aryl compounds as organic electrophiles for carbon–carbon bond formation via cross coupling promoted by group 10 transition metals. The literature provides a wealth of examples demonstrating palladium-catalyzed coupling between organometallic species with popular substrates such as aryl halides,[2] aryl triflates,[3] aryl fluoroalkanesulfonates,[4] and aryl diazonium salts.[5]

The effectiveness of these previous substrates in the cross-coupling reaction prompted us to evaluate related reactions of the little used aryl fluorosulfonate esters **1a–g**. Historically, the fluorosulfonate moiety was utilized as a "super sulfate" leaving group in order to study the formation of the elusive aryl cation species.[6] However, from an experimental point of view, fluorosulfonates never gained popularity due to undesirable methods of preparation and the instability of fluorosulfonic acid, a problem that does not exist with triflic acid.

Aryl fluorosulfonates were first reported in 1930 and were prepared by pyrolysis of arenediazonium fluorosulfonate salts[7] (eq 1). More recenty, such compounds

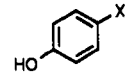
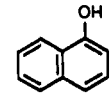
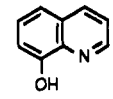
(1)

$Z = N_2^+OSO_2F^-$ (heat, 10% yield), OH ($ClSO_2F$, 15% yield)

have been prepared by reaction of phenols with fluorosulfuryl chloride in the presence of pyridine.[8] Both methods require forcing conditions using difficult to handle reagents and furnish the desired products in low to modest yield.

Table I. Preparation of Aryl Fluorosulfonates

$$ArOH + (FSO_2)_2O \xrightarrow[-78\ °C,\ 2\ h]{i\text{-}Pr_2NEt,\ CH_2Cl_2} ArOSO_2F$$

ArOH	X	yield[a] (%)	compd
		95	**1a**
	H	95	**1b**
	OCH_3	80	**1c**
	Br	75	**1d**
	NO_2	82	**1e**
		94	**1f**
		67	**1g**

[a] Isolated yield of pure product.

Results and Discussion

Since its initial preparation in 1951,[9,10] relatively few reactions involving fluorosulfonic anhydride ($(FSO_2)_2O$) with organic substrates have been reported. Typical uses of this reagent include the bulk polymerization of tetrahydrofuran to give poly(tetramethylene) ether glycol and the self-condensation of a variety of ketones, as well as an isolated example of its reaction with phenol to furnish **1b**

(1) Present address: Bristol-Myers Squibb Pharmaceutical Research Institute, 5 Research Parkway, Wallingford, CT 06492-7660.

(2) For some examples, see: McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422. Bailey, T. R. *Tetrahedron Lett.* **1986**, *27*, 4407. Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.

(3) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. Martorell, G.; Garcia-Raso, A.; Saa, J. M. *Tetrahedron Lett.* **1990**, *31*, 2357. Ohe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1990**, 221. Fu, J. M.; Snieckus, V. *Tetrahedron Lett.* **1990**, *31*, 1665.

(4) Chen, Q. Y.; Yang, Z. Y. *Tetrahedron Lett.* **1986**, *27*, 1171.

(5) Kikukawa, K.; Kono, K.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1983**, *48*, 1333.

(6) For a review of sulfonate leaving groups and related chemistry, see: Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(7) Lange, W.; Mueller, E. *Ber. Dtsch. Chem. Ges. B* **1930**, *63*, 2653.

(8) Cramer, R.; Coffman, D. D. *J. Org. Chem.* **1961**, *26*, 4164.

(9) Hayek, E.; Koller, W. *Monatsh. Chem.* **1951**, *26*, 942. Boudakian, M. M.; Hyde, G. A.; Kongpricha, S. *J. Org. Chem.* **1971**, *36*, 940.

(10) Most preparations of perfluoroalkanesulfonic anhydrides call for the condensation of 2 equiv of the appropriate acid in the presence of phosphorus pentoxide; however, this procedure does not work in the preparation of $(FSO_2)_2O$. We have routinely prepared kilogram batches of the above reagent utilizing the method described by Kongpricha and co-workers involving dehydration in the presence of cyanuric chloride. The desired anhydride is formed in nearly quantitative yield and is a stable, slow to hydrolyze, low-boiling liquid (50 °C) that can be used in a manner similar to that of triflic anhydride: Kongpricha, S.; Preusse, W. C.; Schwarer, R. *Inorg. Synth.* **1968**, *11*, 151.

0022-3263/91/1956-3493$02.50/0

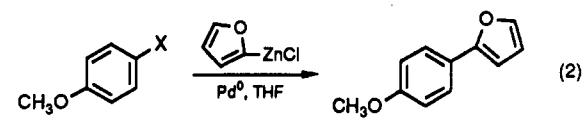
in an unimpressive 23% yield.

We wish to report that a wide variety of aryl and heteroaryl fluorosulfonate esters can be easily prepared using mild conditions and in excellent yield. A variety of phenols, which have been deprotonated with a tertiary amine base at −78 °C in methylene chloride, can be treated with $(FSO_2)_2O$ to furnish the desired aryl fluorosulfonate as illustrated in Table I.

From a preparative point of view, we have found this "triflate alternative" to be cost effective since the parent fluorosulfonic acid costs only a fraction of that for triflic acid (in multigram quantities). As a word of caution, it has been claimed that this compound exhibits an inhalation toxicity on the same order as that of phosgene and is reported as being lethal to rats at 10 ppm constant level during a 4-h exposure period;[11] we report no difficulties handling this reagent either neat or as a molar solution in dichloromethane.

With a variety of easily prepared aryl fluorosulfonates at our disposal, the next challenge was to explore the scope and utility of the fluorosulfonate moiety as an alternative to triflate in several typical palladium-mediated coupling reactions. Two different types of nucleophilic components were evaluated, that is, organozinc chlorides and organostannanes.

Recently, a high-yield synthesis of 2-arylfurans appeared in the literature that relied on the cross coupling of aryl bromides[12] or aryl triflates[13] with the 2-furylzinc chloride as illustrated in eq 2.



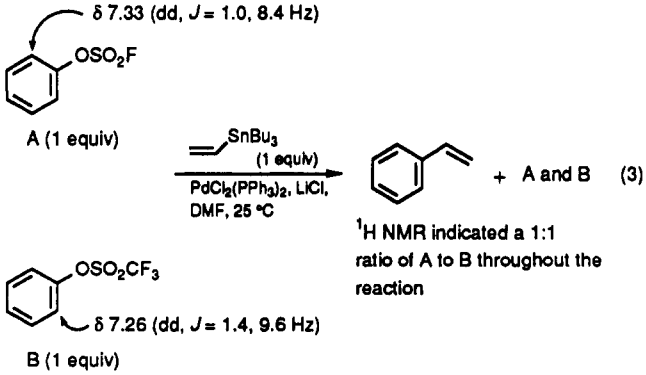
X = Br (69%), OSO_2CF_3 (41%) (2)

It a pleasure to report that both 2-arylfurans as well as several biaryls can be synthesized via cross coupling with the appropriate organozinc chloride and aryl fluorosulfonate. Table II summarizes the results of this study.

A comparison of entry **2b** with the data shown in eq 2 serves to illustrate the *effectiveness of the fluorosulfonate moiety as an electrophilic (acceptor) component* in the cross-coupling reaction. Several biaryls (entries **2e–g**) were also prepared in good yield by reaction with phenylzinc chloride as the nucleophilic (donor) partner. Although the quinoline biaryl **2g** was readily formed, reaction of **1g** with 2-furylzinc chloride (entry **2d**) did not afford the desired 8-substituted quinoline, but rather the disubstituted product shown.

Although the desired coupling did occur, the reaction proceeded with subsequent 1,2-addition to the center adjacent to the quinoline nitrogen (perhaps by coordination of palladium with nitrogen, thus giving that bond partial iminium character). Similar reactions whereby the addition of vinyl and allyl Grignards to quinoline followed by hydrolysis and rearomatization to produce 2-substituted quinolines have been previously reported.[14]

The more popular cross coupling of organostannane reagents with aryl halides or aryl triflates is well documented[15] and has been shown to be a highly effective method for carbon–carbon bond formation. The key role that substituted triflates play in this reaction prompted us to study the behavior of fluorosulfonates **1a–g** under similar reaction conditions. A simple competition study was set up (eq 3) in order to determine the relative rate of reactivity of phenyl fluorosulfonate in comparison to that of phenyl triflate.

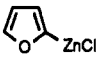
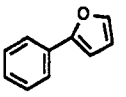
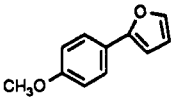
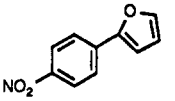
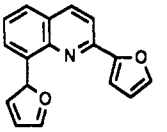
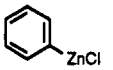
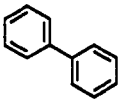
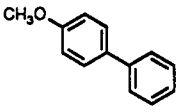
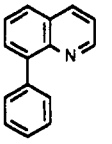


(3)

In this experiment, equimolar amounts of **1b** and phenyl triflate were treated according to the general reaction conditions with 0.5 equiv of vinylstannane. Several reactions were run with end times between 30 min and 6 h, with the reaction generally being complete (50% formation of styrene) within 3 h at ambient temperature. In all instances, proton NMR analysis using the integration values for the protons adjacent to the sulfonyl moiety indicated a residual 1:1 mixture of the starting materials.

Table II. Cross-Coupling Reactions with Organozinc Chlorides[a]

$$ArOSO_2F \xrightarrow[Pd^0,\ THF,\ 50\ °C]{R\text{-}ZnCl} ArR$$

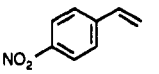
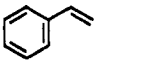
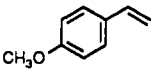
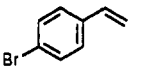
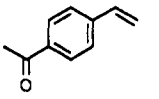
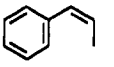
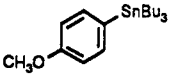
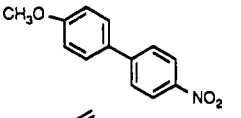
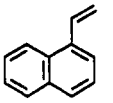
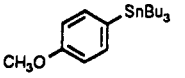
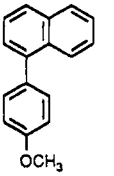
entry	$ArOSO_2F$	RZnCl	product	yield[b] (%)
2a	**1b**			83
2b	**1c**			54
2c	**1e**			80
2d	**1g**			47
2e	**1b**			95
2f	**1c**			56
2g	**1g**			70

[a] THF, 3 equiv of LiCl, 5 mol % $Pd(PPh_3)_4$, 50 °C, 1.5 equiv of RZnCl, 12 h. [b] Isolated yield of pure product.

(11) Muetterties, E. L.; Coffman, D. D. *J. Am. Chem. Soc.* **1958**, *80*, 5914.
(12) Pelter, A.; Rowlands, M.; Clements, G. *Synthesis* **1987**, *51*.
(13) Arcadi, A.; Burini, A.; Cacchi, S.; Delmastro, M.; Marinelli, F.; Pietroni, B. *Synlett* **1990**, 47.
(14) Eisch, J. J.; Comfort, D. R. *J. Org. Chem.* **1975**, *40*, 2288.
(15) For a review see: Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

Table III. Cross-Coupling Reactions with Organostannanes[a]

$$ArOSO_2F \xrightarrow[Pd^0, DMF, LiCl]{R\text{-}SnBu_3} ArR$$

entry	$ArOSO_2F$	stannane	product	yield[b] (%)
3a	**1e**			85 (60)
3b	**1b**			80 (76)
3c	**1c**			75 (70)
3d	**1d**			70 (68)
3e	**1a**			75 (70)
3f	**1b**			82 (70)[c]
3g	**1e**			60 (50)
3h	**1f**			92 (91)
3i	**1f**			75 (69)

[a] DMF, 3 equiv of LiCl, 5 mol % $(PPh_3)_2PdCl_2$, 1.2 equiv of stannane, 25 °C, 6–18 h. [b] Actual yields determined by NMR are reported, isolated yields of pure product given in parentheses. [c] No evidence of the *E* isomer by ^1H NMR.

In light of this, we concluded that the aryl fluorosulfonate couples at a rate identical with that of triflate. With this information a variety of coupling experiments were performed, and the results are summarized in Table III.

While the presence of a halide source such as LiCl or $ZnCl_2$ is essential for coupling to occur, we find that DMF as solvent works quite well and that the reactions proceed at ambient temperature rather than that of refluxing dioxane (98 °C).[3] The cross-coupling reaction of aryl fluorosulfonates with vinylstannanes gave excellent yields of styrene derivatives (entries **3a–e**) and proceeded with retention of double-bond geometry (entry **3f**). Good chemoselectivity can be seen in the case of entry **3d**. In the presence of LiCl, coupling occurred exclusively at the fluorosulfonate center rather than at the bromide. Although the reactions proceeded with excellent yields, we found some difficulty in obtaining high recovery for several of the styrene derivatives. Effective removal of the chlorotributyltin byproduct proved troublesome. Two methods were evaluated by proton NMR integration values. Treatment of the crude reaction mixture with 10% aqueous potassium flouride,[16] whereby the original organotin halide is converted to an insoluble organotin fluoride, resulted in only a 48% reduction of the tin chloride byproduct. The alternate method, which works via the same mode of action, calls for treatment with pyridinium fluoride in the presence of excess pyridine.[17] This method gave better results (68% removal), but subsequent chromatography was still necessary. The inherent loss through additional manipulation involving chromatography and/or distillation is reflected in the lower isolated yields.

Conclusion

An efficient, mild procedure for the preparation of a variety of aryl fluorosulfonates has been demonstrated. The reaction is quite mild and is tolerant of a variety of functional groups. Subsequent cross coupling of these sulfonyl esters with organozinc chlorides and a variety organostannanes, in the presence of lithium chloride and a palladium(0) catalyst, allows for efficient carbon–carbon bond formation. The rate of coupling reaction is identical with that for the corresponding aryl triflates and proceeds at room temperature. Initial studies show that carbonylative coupling with organostannanes is also feasible and will be reported in a future publication.[18] Thus, we have demonstrated that the fluorosulfonate moiety can be considered an inexpensive alternative to triflate and a versatile synthetic intermediate.

Experimental Section

Elemental analyses were performed by the Analytical Research Department at Bristol-Myers Squibb. Tetrahydrofuran (THF) was dried over benzophenone ketyl and distilled prior to use. *N,N*-Dimethylformamide (DMF) was dried over 4-Å molecular

(16) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.
(17) Trost, B. M.; Caldwell, C. G.; Murayama, E.; Meissler, D. *J. Org. Chem.* **1983**, *48*, 3252.
(18) Roth, G. P.; Libby, A. H. Work in progress

sieves and stored under nitrogen. Unless otherwise stated, all reactions were run under positive nitrogen pressure. Most reagents were obtained from commercial sources with the exception of fluorosulfonic anhydride, which was prepared according to the procedure described by Kongpricha and co-workers.[10] **CAUTION**: This reagent should be handled with care. Fluorosulfonic anhydride has been reported to have an inhalation toxicity similar to that of phosgene.[11]

General Procedure for Fluorosulfonation. 4-Acetylphenyl Fluorosulfonate (1a). An oven-dried flask containing a magnetic stirring bar was cooled under an inert (N_2) atmosphere and then charged with CH_2Cl_2 (180 mL) and 4-hydroxyacetophenone (10.0 g, 73.4 mmol). The resulting solution was cooled to −78 °C in a dry ice–acetone bath wherein a slurry formed. *N,N*-Diisopropylethylamine (12.8 mL, 73.4 mmol) was added dropwise over a 5-min period, and the resulting pale yellow solution was stirred for 20 min. Fluorosulfonic anhydride (13.38 g, 73.4 mmol) was then added dropwise over 10 min, and the nearly colorless solution was stirred for an additional 30 min before addition of water (25 mL). The reaction was allowed to warm to ambient temperature then the organic fraction was washed sequentially with dilute HCl, dilute NaOH, and water. The organic fraction was then dried ($MgSO_4$) and concentrated to give a pale yellow oil. Purification by bulb-to-bulb distillation (120 °C (0.1 mm)) furnished 15.2 g (95%) of the desired product as a waxy colorless solid, mp 30 °C: IR (film) 1697, 1594, 1462, 1264, 1233, 1144, 925, 910, 848, 609 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.06 (d, 2 H, J = 9.0 Hz), 7.43 (dd, 2 H, J = 1.2, 8.8 Hz), 2.61 (s, 3 H); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 197.2, 152.7, 137.0, 130.7, 121.5, 26.6. Anal. Calcd for $C_8H_7FO_4S$: C, 44.03; H, 3.23. Found: C, 44.34; H, 3.37.

Phenyl Fluorosulfonate (1b). As described in the general procedure, phenol was converted to the corresponding fluorosulfonate (95%): colorless oil from bulb-to-bulb distillation (178 °C (760 mm) [lit.[9] 180 °C (760 mm)]; ^1H NMR (360 MHz, $CDCl_3$) δ 7.50–7.35 (complex m, 3 H), 7.33 (dd, 2 H, J = 1.0, 8.4 Hz); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 150.1, 130.4, 128.7, 120.9.

4-Methoxyphenyl Fluorosulfonate (1c). 4-Methoxyphenol was converted to the corresponding fluorosulfonate according to the general procedure (80%): colorless oil obtained from bulb-to-bulb distillation (95 °C (0.25 mm)); IR (film) 1501, 1447, 1233, 1169, 913 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.25 (d, 2 H, J = 9.2 Hz), 6.93 (d, 2 H, J = 9.2 Hz), 3.82 (s, 3 H); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 159.3, 143.6, 121.9, 115.2, 55.7. Anal. Calcd for $C_7H_7FO_4S$: C, 40.77; H, 3.43. Found: C, 41.01; H, 3.42.

4-Bromophenyl Fluorosulfonate (1d). 4-Bromophenol was converted to the desired fluorosulfonate according to the general procedure (75%): colorless oil obtained from bulb-to-bulb distillation (90 °C (0.3 mm)); IR (film) 1481, 1454, 1236, 1175, 1145, 915, 582 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.60 (d, 2 H, J = 9.0 Hz), 7.23 (d, 2 H, J = 8.5 Hz); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 148.9, 133.6, 122.7, 122.4. Anal. Calcd for $C_6H_4BrFO_3S$: C, 28.25; H, 1.58. Found: C, 28.30; H, 1.82.

4-Nitrophenyl Fluorosulfonate (1e). 4-Nitrophenol was converted to the desired fluorosulfonate according to the general procedure (82%): pale yellow oil obtained from bulb-to-bulb distillation (130 °C (0.3 mm)); IR (film) 1533, 1487, 1457, 1353, 1238, 1150, 914, 586 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.39 (d, 2 H, J = 9.2 Hz), 7.57 (d, 2 H, J = 8.8 Hz); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 153.4, 147.4, 126.2, 122.23. Anal. Calcd for $C_6H_4FNO_5S$: C, 32.58; H, 1.83. Found: C, 32.52; H, 2.08.

1-[(Fluorosulfonyl)oxy]naphthalene (1f). Following the general procedure, 1-naphthol (2.0 g, 13.8 mmol) furnished 2.9 g (94%) of the desired product as a colorless oil after purification by bulb-to-bulb distillation (135 °C (0.25 mm)): IR (film) 1604, 1509, 1451, 1236, 1210, 919, 768 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.08 (d, 1 H, J = 8.0 Hz), 7.92–7.87 (m, 2 H), 7.67–7.46 (complex m, 3 H), 7.55–7.48 (complex m, 2 H); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 146.1, 134.8, 128.7, 128.1, 127.8, 127.4, 125.7, 125.1, 120.5, 117.5. Anal. Calcd for $C_{10}H_7FO_3S$: C, 53.09; H, 3.11. Found: C, 53.59; H, 3.12.

8-[(Fluorosulfonyl)oxy]quinoline (1g). 8-Hydroxyquinoline was converted to the corresponding fluorosulfonate according to the general procedure (67%): colorless solid from hexane–ether; mp 66–67 °C; IR (KBr) 1447, 1297, 1069, 1048, 1023, 921, 851 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 9.03 (dd, 1 H, J = 1.6, 4.2 Hz), 8.21 (dd, 1 H, J = 1.6, 8.4 Hz), 7.87 (dd, 1 H, J = 1.1, 8.4 Hz), 7.73 (d, 1 H, J = 7.7 Hz), 7.59–7.50 (m, 2 H); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 151.8, 145.8, 140.3, 135.9, 129.9, 128.7, 125.8, 122.7, 121.3. Anal. Calcd for $C_9H_6FNO_3S$: C, 47.56; H, 2.67. Found: C, 47.26; H, 2.52.

Cross-Coupling Reactions with Phenyl- and 2-Furylzinc Chloride. 2-Phenylfuran (2a). General Procedure. A solution of furan (136 mg, 2.0 mmol) in THF (3 mL) was cooled to −78 °C in a dry–acetone bath and treated with *n*-butyllithium (2.5 M in hexane, 0.8 mL, 2.0 mmol). The resulting colorless solution was allowed to warm to 0 °C and held at that temperature for 1 h. An ether solution of zinc chloride (1 M, 2.0 mL, 2.0 mmol) and then added, and the resulting solution was allowed to stir at ambient temperature for at least 30 min prior to use.

For reactions involving cross coupling with phenylzinc chloride, the following procedure was utilized for the preparation of the organometallic partner. A THF solution of zinc chloride (1.5 equiv, 1 M in ether) was cooled to 0 °C in an ice bath and subsequently treated with phenyllithium (1.5 equiv, 2 M in cyclohexane–ether). The resulting suspension was allowed to stir for at least 30 min prior to use.

A separate flask equipped with a magnetic stirring bar and reflux condenser was charged with phenyl fluorosulfonate (300 mg, 1.7 mmol) and THF (6 mL). To this solution was then added $Pd[P(C_6H_5)_3]_4$ (98 mg, 0.085 mmol), resulting in a light orange solution. The furylzinc chloride solution prepared previously was then transferred via syringe, and the resulting pale yellow solution was heated at 50 °C (oil bath) for 12 h. Dilute hydrochloric acid (10 mL; 0.1 M) was then added to the cooled reaction mixture followed by ether (20 mL). The aqueous layer was separated and back-extracted with additional ether. The combined organic fractions were washed with water then dried ($MgSO_4$) and concentrated to give a crude brown oil. Bulb-to-bulb distillation [72–75 °C (2.5 mm) (lit.[12] 74–76 °C (2.5 mm))] afforded 203 mg (83%) of the desired product as a colorless oil. Yields of products synthesized by this methodology are listed in Table II.

Cross-Coupling Reactions with Organostannanes. 4-Nitrostyrene (3a). General Procedure. To a stirred solution of 4-nitrophenyl fluorosulfonate (221.1 mg, 1.0 mmol) in DMF (4.5 mL) was added LiCl (126.9 mg, 3.0 mmol) and vinyltributylstannane (380.5 mg, 1.2 mmol). The resulting solution was stirred for 5 min then was treated with $(Ph_3P)_2PdCl_2$ (35.1 mg, 0.05 mmol). The mixture was sampled periodically for evaluation by HPLC. When the HPLC data indicated the reaction was complete, workup consisted of quenching the reaction with water (25 mL) and extraction with ethyl acetate (3 × 20 mL). The combined organic fractions were dried ($MgSO_4$) and concentrated to give the crude product. Following column chromatography (hexane), the semipure product was isolated by bulb-to-bulb distillation as a pale yellow oil (60%); the isolated product rapidly decomposed. Yields of products synthesized by this methodology are listed in Table III.

Registry No. **1a**, 133042-62-3; **1b**, 330-00-7; **1c**, 775-27-9; **1d**, 133042-63-4; **1e**, 51451-34-4; **1f**, 133042-64-5; **1g**, 133042-65-6; **2a**, 17113-33-6; **2b**, 17113-31-4; **2c**, 28123-72-0; **2d**, 133042-66-7; **2e**, 92-52-4; **2f**, 613-37-6; **2g**, 605-04-9; **3a**, 100-13-0; **3b**, 100-42-5; **3c**, 637-69-4; **3d**, 2039-82-9; **3e**, 10537-63-0; **3f**, 766-90-5; **3g**, 2143-90-0; **3h**, 826-74-4; **3i**, 27331-33-5; Ac-*p*-C_6H_4OH, 99-93-4; PhOH, 108-95-2; MeO-*p*-C_6H_4OH, 150-76-5; Br-*p*-C_6H_4OH, 106-41-2; NO_2-*p*-C_6H_4OH, 100-02-7; $(FSO_2)_2O$, 13036-75-4; PhLi, 591-51-5; H_2C=$CHSnBu_3$, 7486-35-3; H_3CCH=$CHSnBu_3$, 66680-84-0; MeO-*p*-$C_6H_4SnBu_3$, 70744-47-7; $ZnCl_2$, 7646-85-7; $Pd[P(C_6H_5)_3]_4$, 14221-01-3; $(Ph_3P)_2PdCl_2$, 13965-03-2; LiCl, 7447-41-8; FSO_2OH, 7789-21-1; 1-naphthol, 90-15-3; 8-quinolinol, 148-24-3; furan, 110-00-9; cyanuric chloride, 108-77-0.