J. Org. Chem. **1993**, *58*, 1963-1966

Palladium-Catalyzed Cross-Coupling Synthesis of Hindered Biaryls and Terphenyls. Cocatalysis by Copper(I) Salts

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Received September 29, 1992

The biaryl unit is present in many natural products, and more interestingly, biaryls and higher analogs are basic building blocks in many newly designed materials.[1] With the purpose of preparing large polyaryls with restricted rotation at some points of the chain for materials science, we decided to look for efficient conditions to synthesize highly hindered biaryls and teraryls.

The transition metal catalyzed formation of aryl–aryl bonds[2] appeared to be ideally suited for the preparation of biaryls[3] and higher oligomers such as teraryls, quateraryls, etc.[4]

In our approach to this subject we choose the Stille reaction,[5] i.e. the palladium-catalyzed cross-coupling reaction between phenol triflates and aryl stannanes, because (1) monohydric, dihydric and higher polihydric phenols are readily available substances and (2) simple derivatives such as halogenated phenols or polyphenols might be useful substrates for preparing mixed polyarylic materials, provided that regioselective reactions could be achieved.[5]

Prompted by the enormous flow of recent work on the subject[6] we like to report herein that our previously reported methodology which gives poor results for the cross coupling reactions of highly hindered, electron-rich phenol triflates[7] can be substantially improved by using a Cu(I) salt as cocatalyst. In particular, herein we describe (a) the synthesis of highly hindered 2,2′,6-trisubstituted and 2,2′,6,6′-tetrasubstituted biaryls[8] and (b) the preparation of terphenyls starting from either hydroquinone ditriflate or the triflate of 4-bromophenol and the appropriate arylstannane. It should be emphasized that neither arylboronic acids nor arylzinc compounds have been employed for comparison for our plans.[8]

Considerable work was done in optimizing the experimental conditions (catalyst, phosphine, stannane, copper(I) halide, solvent, and temperature) for the preparation of both biaryls or teraryls. The following key points which derive from the present work should be kept in mind for success in Stille-type cross-couplings as applied to hindered substrates and reagents: 1. Add a copper (I) salt as cocatalyst. Several authors[9] have recently reported the beneficial effects of adding copper salts to the reaction mixture, although their actual role in the cross-coupling reactions is as yet unknown.[10] In our experience, either CuBr or CuI can be employed (2–4 equiv relative to palladium) as only minor changes in yield (ca. 10%) have been noticed when using one or another as cocatalyst. 2. Employ an excess of stannane (portionwise added) for optimum yield as it appears to be partially destroyed in the presence of copper salts. 3. No generalization can be made in regard with the use of phosphines. Best choice of phosphine (if any) should be decided on a case by case basis. The use of triphenylarsine led to some improvement in one isolated case. Further research is needed. 4. Whereas DMF works best for preparing highly encumbered biaryls and teraryls from aryl triflates or bromo aryl triflates (method A), dioxane is the best choice for cross-couplings with hydroquinone ditriflates (method B).

As illustrated in Table I, by using method A or B, encumbered products having one or two biaryl bonds can be made in a one-pot reaction. Yields of the cross-coupling reactions appear to be very sensitive to the steric hindrance of the arylstannane moiety as defined by the presence of ortho substituents in the aryl group. For comparison purposes, those obtained with the old methodology[7a] are given in Table I, where appropriate. The case of ester **1d** is worthy of note because of its reluctance to undergo cross-coupling in the absence of Cu(I) salts. Actually, biaryl **5d** could be obtained in 30% yield only when working in the presence of a copper(I) salt.[11] This difficulty in preparing a 2,2′,6-trisubstituted biarylic ester needs to be mentioned because (a) **1d** undergoes efficient cross-couplings with allyl- and phenylstannanes[7a] and (b) other closely related substrates have been reported to react with the phenyltributylstannane thus giving rise to the corresponding 2,2′-disubstituted biarylic esters in high yield.[12]

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(1) See, for example: Miller, T. M.; Neenan, T. X., Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018. Wallow, T. I.; Nowak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7064. Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592. Zhou, Z.-h.; Maruyama, T.; Kanbara, T.; Ikeda, T.; Ichimura, K.; Yamamoto, T.; Tokuda, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1210. See also: Scherf, U.; Müllen, K. *Synthesis* **1992**, 23 and references cited therein. See also refs 2–5 cited in ref 4a.

(2) For a recent, comprehensive review on the subject see: Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977. See also: Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.

(3) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139. Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613. Tomao, K.; Sumitami, K.; Zembayashi, M.; Funoka, A.; Kodama, S.; Nakayima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958. Meyers, A. I.; Gabel, R.; Mihelich, E. D. *J. Org. Chem.* **1978**, *43*, 1372. Lipshutz, B. H.; Siegmann, K.; García, E. *J. Am. Chem. Soc.* **1991**, *113*, 8161. Du, C.-J. F.; Hart, H.; Ng, K. K. D. *J. Org. Chem.* **1986**, *51*, 3162. Elmory, S. S.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1991**, *32*, 4175. See also ref 2.

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(8) 2,2′,6-Trisubstituted and 2,2′,6,6′-tetrasubstituted biaryls can be customarily obtained by the Meyers cross-coupling method, although, here too, steric crowding severely affects the yield. See, for example: Meyers, A. I.; Himmelsbach, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 682. Meyers, A. I.; Meier, A.; Rawson, D. J. *Tetrahedron Lett.* **1992**, *33*, 853 and references cited therein. Cross-couplings of aryl halides or triflates with hindered arylboronic acids or aryltin or arylzinc compounds have been shown to be highly dependant on the steric hindrance of the organometallic component. For some recent examples, see: Kelly, T. R.; Kim, M. H. *J. Org. Chem.* **1992**, *57*, 1593 and ref 9b and c. See, however: Widdowson, D. A.; Zhang, Y.-Z. *Tetrahedron* **1986**, *42*, 2111.

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(10) Added copper may facilitate the transmetalation step. See ref 9a and references cited therein.

(11) A 20% yield of **5d** was obtained by using the reported method[7a] provided that excess palladium catalyst (20%) is used.

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Table I. Palladium–Copper-Cocatalyzed Synthesis of Encumbered Biaryls and Terphenyls

entry	triflate	stannane	product	yield (%)	method [phosphine]
1	**1a**	**2**	**5a**	49(41)[a]	A[PPh$_3$]
2	**1b**	**2**	**5b**	93(64)[a]	A[none]
3	**1c**	**2**	**5c**	94(57)[a]	A[none]
4	**1d**	**2**	**5d**	30(0)[a]	A[PPh$_3$]
5	**1b**	**3a**	**6b**	26	A[PPh$_3$]
6	**1b**	**3b**	**6b**	13	A[PPh$_3$]
7	**1e**	**3a**	**6e**	25	A[P(o-MePh)$_3$]
8	**10**	**4a**	**11a**	62	A[PPh$_3$]
9	**10**	**4b**	**11b**	93	A[PPh$_3$]
10	**10**	**4c**	**11c**	21	A[AsPh$_3$]
11	**8**	**4a**	**11a**	47	B[PPh$_3$]
12	**8**	**4b**	**11b**	66	B[PPh$_3$]
13	**8**	**4c**	**11c**	11	B[PPh$_3$]

[a] *Yield obtained by the reported method.*[7a]

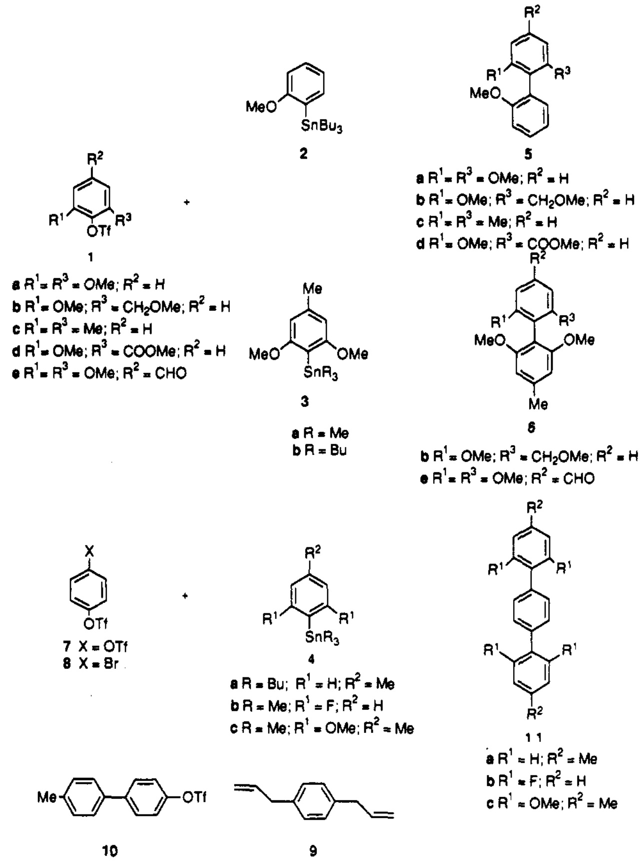
Typical byproducts found (GC/MS detected) in these reactions are the biaryls Ar–Ar presumably deriving from homocoupling of the stannane ArSnR$_3$. Other byproducts such as Ar-Φ, as well as the toluene Ar′-Me (when ArSnMe$_3$ is used) and Ar′-H or Ar′-Bu (when a tributylstannane such as **3b** was used) were also observed.

Highly hindered 2,2′,6,6′-substituted biaryls **6b** and **6e** were isolated in low yield from the complex reactions mixtures after repeated chromatography. Actually, Ar′-Me was usually found to be the major product of the reactions of stannane **3a** with either **1b** or **1e**. All attempts at minimizing these undesired reactions by employing stannane **3b** instead of **3a** led to no improvement, byproducts of the type Ar′-H (major) and Ar′-Bu (minor) now becoming the most important products. To the best of our knowledge, this is the first synthesis, though in low yield, of 2,2′,6,6′-substituted biaryls through an intermolecular, palladium–copper-cocatalyzed biarylic cross-coupling reaction (Scheme I).[13]

Hydroquinone ditriflates were first employed for our planned synthesis of terphenyls and higher homologues. Hydroquinone ditriflate was tested for coupling with common stannanes such as allyltributylstannane so as to check its reactivity. Although ditriflate **7** was found to react more slowly than common phenol triflates, diallylbenzene **9** could be obtained in high yield after some experimentation varying the catalyst, cocatalyst, and the phosphine employed (see Experimental Section for details).

Unfortunately, reaction of ditriflate **7** with arylstannanes **4a** under the above conditions (even when using a copper(I) salt as cocatalyst) led to a very complex mixture of products from which the desired 4,4″-dimethyl-*p*-terphenyl **11a** could be isolated in very low yield (<10%) after extensive chromatography.

Scheme I



Therefore, we turned our attention to a stepwise approach using the triflate of 4-bromo phenol **8** (or related substrates) as starting material. In principle, this plan should have the added advantage, reported by Stille and Echavarren,[5a] of the different reactivity of the aryl triflate and aryl halide moieties which can be tailored by appropriate control of the reaction conditions. Regioselective cross-coupling at the aryl bromide center was carried out by using slightly modified (external phosphine and a copper(I) salt added) reported conditions (tetrakis(triphenylphosphine)palladium in refluxing dioxane, in the absence of added lithium chloride).[5a] The desired biaryl triflate **10** was isolated in 89% yield. Curiously enough, terphenyl **11a** was detected as a minor byproduct (ca. 10% yield) together with **10** (70% yield) when working in refluxing DMF, instead of dioxane, thus suggesting that ion pair solvation is an important factor in controlling the overall rate of reaction at the triflate center. In other words, it appears as if the rate of triflate chloride (or bromide) exchange, prior to the transmetalation step, is solvent dependent.

The above observation led us to devise a one pot method for obtaining terphenyls from either bromophenol triflate **8** or hydroquinone ditriflate **7**. As illustrated in Table I, terphenyls **11a**, and **11b** were obtained in medium to good isolated yields from bromophenol triflate **8** and organostannanes **4a** and **4b** (method A) by simply operating in refluxing DMF in the presence of added lithium chloride. As expected, the use of a hindered stannane such as **4c** further lowered the yield of the desired terphenyl **11c** which was obtained in only 11% yield. The use of triphenylarsine[14] led to some improvement as **11c** was now obtained in 21% yield.

These terphenyls were also obtained, although in somewhat lower yield, by reacting hydroquinone ditriflate **7** with organostannanes **4a**, **4b**, and **4c** in refluxing dioxane (method B).

In summary, the synthesis of highly encumbered 2,2′,6-trisubstituted and even 2,2′,6,6′-tetrasubstituted biaryls as well as terphenyls can be achieved by palladium–copper-cocatalyzed cross-coupling between an aryl triflate or hydroquinone ditriflate and the appropriate organostannane. Reaction yield is very sensitive to steric hindrance.

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Fine tuning of such reaction variables as the palladium catalyst, the phosphine (or arsine), and the solvent used is recommended for final yield optimization.

Experimental Section

General Methods. All melting points are uncorrected and were taken on a capillary melting point apparatus. The boiling points given refer to those observed on bulb-to-bulb distillation. Proton NMR spectra were obtained on a 300-MHz spectrometer in $CDCl_3$ (unless otherwise noted). Electron impact mass spectra were recorded at 70 eV ionizing energy. Column chromatography was performed on silica gel Merck (Kieselgel 40). Commercial dry DMF, phenols, and stannanes were used as received from Aldrich. Tributyl(*o*-methoxyphenyl)stannane,[15] trimethyl(2,6-dimethoxy-4-methylphenyl)stannane,[9c] trimethyl(2,6-difluorophenyl)stannane,[9c] and tributyl(*p*-methylphenyl)stannane[16] were prepared as reported. All phosphines were employed as received. The abbreviation 1-dppf stands for 1,1′-bis(diphenylphosphino)ferrocene. Dry LiCl was prepared by heating the commercial sample in vacuo (0.1 mmHg) at 100 °C for 6 h. The purity of all compounds for which no elemental analysis is provided was judged to be >95% by ^{13}C and ^{1}H NMR (supplementary material).

Aryl Triflates. 2,6-Dimethoxyphenyl trifluoromethanesulfonate[7] (**1a**), 2-methoxy-6-(methoxymethyl)phenyl trifluoromethanesulfonate[7] (**1b**), 2,6-dimethylphenyl trifluoromethanesulfonate[7] (**1c**), 2-methoxy-6-(methyloxycarbonyl)phenyl trifluoromethanesulfonate[7] (**1d**), 4-formyl-2,6-dimethoxyphenyl trifluoromethanesulfonate[7] (**1e**), and *p*-bromophenyl trifluoromethanesulfonate[5a] (**8**) were prepared as previously reported. 1,4-Bis[(trifluoromethanosulfonyl)oxy]benzene (**7**) was prepared analogously.[7]

1,4-Bis[(trifluoromethanosulfonyl)oxy]benzene (7) was obtained in 86% yield as a transparent oil, which slowly solidified: mp 52–53 °C; IR (film) 3150, 1500, 1430, 1220, 1140, 1000, 900, 860, 710 cm^{-1}; ^{1}H NMR δ 7.40 (s, 4 H) ppm; ^{13}C NMR δ 148.39, 123.45, 118.13 (q, J = 320.4 Hz) ppm; EIMS *m/e* 374 (M$^+$, 14), 241 (26), 177 (93), 149 (63), 101 (10), 83 (18), 82 (18), 69 (100). Anal. Calcd for $C_8H_4F_6O_6S_2$: C, 25.67; H, 1.07. Found: C, 25.72; H, 1.25.

Palladium-Copper Cocatalyzed Cross-Couplings of Hindered Aryl Triflates and Bromoaryl Triflates with Hindered Organostannanes. General Procedure (Method A). A round-bottom flask was charged with a mixture of 0.5 mmol of triflate **1** or **8**, anhydrous LiCl (4 mmol), the appropriate phosphine (0.15–0.2 mmol), CuBr (0.2 mmol), and $PdCl_2(PPh_3)_2$ (10–20 mol %) suspended in DMF (2.5 mL). The organostannane **2**, **3**, or **4** (1–1.5 mmol) was added to the mixture (best results were obtained by addition of stannane in two portions, i.e., at the beginning of the reaction and at half completion). A crystal of inhibitor (2,6-di-*tert*-butyl-4-methylphenol) was added, and the mixture was then heated to reflux, under Ar, during 8–24 h. Water and ether (25 mL) were added, and the organic phase was washed subsequently with 1.5 N HCl (6 × 20 mL), a saturated solution of potassium fluoride (5 × 20 mL), and finally dried over Na_2SO_4. Evaporation to dryness furnished a residue which was suspended in ethyl acetate and filtered off. The filtrate was evaporated, and the resulting crude material purified by column chromatography (*n*-hexane–ethyl acetate). Final crystallization or bulb-to-bulb distillation usually furnished pure products (Table I).

Palladium–Copper-Cocatalyzed Cross-Couplings of Hydroquinone Ditriflate with Organostannanes. General Procedure (Method B). A round-bottom flask was charged with a mixture of 0.5 mmol of triflate **7**, anhydrous LiCl (8 mmol), PPh$_3$ (0.2 mmol), CuBr (0.2 mmol), and Pd(PPh$_3$)$_4$ (20 mol %) suspended in dioxane (4 mL). A crystal of inhibitor (2,6-di-*tert*-butyl-4-methylphenol) was added and the mixture heated to reflux, under Ar, during 3–10 h. The organostannane **4** (2 mmol) was added to the mixture in two portions (at the beginning of the reaction and at half-completion). Workup as in method A furnished **11a**, **11b**, and **11c** as shown in Table I.

2,2′,6-Trimethoxybiphenyl (5a) was obtained in 49% yield (method A, 0.2 mmol of PPh$_3$) as a white solid, mp 132–34 °C.[7a]

2,2′-Dimethoxy-6-(methoxymethyl)biphenyl (5b) was obtained in 93% yield (method A, no external phosphine added) as a white solid: oil, bp 115–20 °C/0.12 mmHg.[7a]

2,6-Dimethyl-2′-methoxybiphenyl (5c) was isolated in 94% yield (method A, no external phosphine added): oil, bp 95–100 °C/0.12 mmHg.[7a]

2-(Carboxymethyl)-2′,6-dimethoxybiphenyl (5d) was obtained in 30% yield (method A, 0.4 mmol of PPh$_3$) as a solid: mp 103–105 °C; IR (film) 2940, 2920, 2870, 1720, 1580, 1450, 1300, 1250, 1100, 650 cm^{-1}; ^{1}H NMR δ 7.47 (dd, 1 H, J = 7.9 and 1.0 Hz), 7.37 (t, 1 H, J = 7.9 Hz), 7.32 (ddd, 1 H, J = 8.3, 7.5 and 1.8 Hz), 7.12 (dd, 1 H, J = 7.5 and 1.7 Hz), 7.11 (d, 1 H, J = 7.9 Hz), 6.99 (t, 1 H, J = 7.5 Hz), 6.94 (d, 1 H, J = 8.3 Hz), 3.74 (s, 3 H), 3.72 (s, 3 H), 3.57 (s, 3 H) ppm; ^{13}C NMR δ 168.26, 157.28, 156.75, 132.98, 130.84, 128.67, 128.26, 127.93, 125.81, 121.61, 120.18, 114.41, 110.63, 56.14, 55.61, 51.73 ppm; EIMS *m/e* 272 (M$^+$, 64), 242 (18), 241 (100), 226 (47), 211 (20), 183 (11), 181 (13), 179 (66), 155 (17), 139 (15), 127 (12); HRMS calcd for $C_{16}H_{16}O_4$ 272.10485, found 272.10600.

2,2′,6-Trimethoxy-6′-(methoxymethyl)-4-methylbiphenyl (6b) was obtained as a solid in 26% yield (method A, 0.2 mmol of PPh$_3$): mp 100–102 °C; IR (film) 2920, 2810, 1570, 1460, 1230, 1120, 1060, 710, 660, 640 cm^{-1}; ^{1}H NMR δ 7.33 (dd, 1 H, J = 8.1 and 7.7 Hz), 7.17 (d, 1 H, J = 7.7 Hz), 6.90 (d, 1 H, J = 8.1 Hz), 6.47 (s, 2 H), 4.16 (s, 2 H), 3.72 (s, 3 H), 3.68 (s, 6 H), 3.22 (s, 3 H), 2.41 (s, 3 H) ppm; ^{13}C NMR δ 157.68, 157.42, 139.09, 128.19, 122.37, 119.18, 110.69, 109.95, 105.53, 105.13, 71.97, 57.89, 56.08, 55.82, 22.31 ppm; EIMS *m/e* 302 (M$^+$, 100), 287 (20), 272 (19), 271 (57), 259 (48), 255 (25), 244 (31), 241 (36), 240 (22), 239 (54), 226 (13), 225 (20), 212 (17), 211 (12), 197 (14), 195 (13), 152 (13), 115 (12); HRMS calcd for $C_{18}H_{22}O_4$ 302.15180, found 302.14970.

4-Formyl-2,2′,6,6′-tetramethoxy-4′-methylbiphenyl (6e) was isolated as a solid in 25% yield (method A, 0.2 mmol of P(*o*-MePh)$_3$, mp 125–6 °C; IR (film) 2920, 2820, 1690, 1560, 1490, 1410, 1300, 1230, 1120, 740, 700 cm^{-1}; ^{1}H NMR δ 9.97 (s, 1 H), 7.17 (s, 1 H), 6.50 (s, 2 H), 3.81 (s, 6 H), 3.72 (s, 6 H), 2.42 (s, 3 H) ppm; ^{13}C NMR δ 192.09, 158.97, 157.77, 139.66, 136.90, 119.81, 108.40, 105.48, 105.42, 56.25, 56.05, 22.36 ppm; EIMS *m/e* 316 (M$^+$, 100), 285 (10), 270 (11), 179 (19), 169 (14), 165 (21), 152 (15), 151 (23), 135 (17), 128 (18), 127 (10), 119 (10), 115 (20), 105 (12), 91 (14); HRMS calcd for $C_{18}H_{20}O_5$ 316.13106, found 316.1328.

A byproduct obtained when using stannane **3a** was **3,5-dimethoxy-4-methylbenzaldehyde**: solid in 33%–45% yield; mp 89–90 °C; IR (film) 2960, 2840, 1680, 1590, 1450, 1390, 1309, 1240, 1180, 730 cm^{-1}; ^{1}H NMR δ 9.91 (s, 1 H), 7.06 (s, 2 H), 3.90 (s, 6 H), 2.16 (s, 3 H) ppm; ^{13}C NMR δ 191.89, 158.66, 135.04, 122.48, 104.60, 55.85, 8.92 ppm; EIMS *m/e* 180 (M$^+$, 100), 179 (30), 151 (22), 149 (13), 121 (17), 107 (10), 91 (32), 79 (11), 77 (26), 65 (11). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 66.89; H, 6.80.

1,4-Bis(4-methylphenyl)benzene (11a) was isolated in 62% (method A, 0.2 mmol of PPh$_3$) or 47% yield (method B): solid; mp 247–9 °C; IR (film) 2960, 2920, 2840, 1570, 1560, 1465, 1280, 1000, 6503 cm^{-1}; ^{1}H NMR δ 7.65 (s, 4 H), 7.55 (d, 4 H, J = 8.2), 7.26 (d, 4 H, J = 8.2 Hz), 2.41 (s, 6 H) ppm; ^{13}C NMR δ 139.76, 137.88, 137.06, 129.51, 127.24, 126.85, 21.11 ppm; EIMS *m/e* 259 (M$^+$ + 1.22), 258 (M$^+$, 100), 257 (14), 241 (6), 183 (5), 165 (7), 165 (21); HRMS calcd for $C_{20}H_{18}$ 258.14084, found 258.1400.

1,4-Bis(2,6-difluorophenyl)benzene (11b) was isolated in 93% (method A, 0.2 mmol of PPh$_3$) or 66% yield (method B): solid; mp 204–5 °C; IR (film) 2800, 1620, 1600, 1590, 1490, 1405, 1200, 1010, 840, 780 cm^{-1}; ^{1}H NMR δ 7.58 (s, 4 H), 7.30 (tt, 4 H, J = 8.1 and 7.2 Hz), 7.01 (dd, 2 H, J = 8.1 and 8.0 Hz) ppm; ^{13}C NMR δ 160.16 (dd, J = 248.9 and 6.8 Hz), 130.89, 130.20 (pseudo-t, J = 2.0 Hz), 129.04 (t, J = 9.8 Hz), 118.02 (t, J = 18.7 Hz), 11.72 (dd, J = 18.1 and 9.1 Hz) ppm; ^{19}F NMR δ 114.5 (t, 4 F, J = 6.7) ppm; EIMS *m/e* 302 (M$^+$, 100), 280 (10), 164 (12), 151 (26), 140 (10), 138 (14), 131 (9). Anal. Calcd for $C_{18}H_{10}F_4$: C, 71.52; H, 3.31. Found: C, 71.50; H, 3.60.

1,4-Bis(2,6-dimethoxy-4-methylphenyl)benzene (11c) was isolated in 21% (method A, 0.2 mmol of AsPh$_3$) or 11% yield

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(method B): solid; mp 212–214 °C; IR (film) 2910, 2840, 1600, 1560, 1460, 1390, 1225, 1020, 1000, 700, 740 cm^{-1}; ^{1}H NMR δ 7.36 (s, 4 H), 6.48 (s, 4 H), 3.74 (s, 12 H), 2.41 (s, 6 H) ppm; ^{13}C NMR δ 157.57, 138.50, 132.11, 130.24, 128.42, 105.06, 55.79, 22.16 ppm; EIMS *m/e* 378 (M$^+$, 100), 348 (11), 189 (39), 165 (20), 158 (15), 150 (11), 149 (16), 143 (11), 128 (10), 122 (12), 108 (11), 101 (13); HRMS calcd for $C_{24}H_{26}O_4$ 378.18310, found 378.1840.

1,4-Diallylbenzene (9) was obtained in 100% yield by heating a mixture of (7) (0.5 mmol) to reflux (3 h) with 2 mmol of tributyl(allyl)stannane, 4 mmol of LiCl, $PdCl_2(PPh_3)_2$ (20 mol %), and 0.4 mmol of 1-dppf (PPh_3 gives a somewhat lower yield) in DMF (4–5 mL). The usual workup[7a] yielded **9** as an oil: bp 105–110 °C/0.12 mm Hg; IR (film) 3080, 2910, 1700, 1600, 1500, 1410, 1260, 1120, 815, 795 cm^{-1}; ^{1}H NMR δ 7.13 (s, 4 H), 5.98 (ddt, 2 H, J = 17.8, 10.1 and 6.7 Hz), 5.09 (dd, 2 H, J = 10.1 and 1.3 Hz), 5.08 (dd, 2 H, J = 17.8 and 1.3 Hz), 3.37 (dd, 2 H, J = 6.7 and 1.3 Hz) ppm; ^{13}C NMR δ 137.78, 137.62, 128.63, 115.65, 39.86 ppm; EIMS *m/e* 158 (M$^+$, 41), 143 (17), 129 (32), 128 (32), 117 (100), 116 (24), 115 (76), 91 (27); HRMS calcd for $C_{12}H_{14}$ 158.10954, found 158.1099.

4-Methyl-4′-[(trifluoromethanesulfonyl)oxy]biphenyl (10) was isolated in 89% yield by refluxing for 2 h a mixture of 0.5 mmol of (8), $PdCl_2(PPh)_3$ (3 mol %), 0.05 mmol of PPh_3, CuBr (0.1 mmol), and 0.6 mmol of stannane **4a** in dioxane (4 mL). The usual workup yielded **10** as a solid: mp 65–6 °C; IR (film) 2950, 2010, 2840, 1700, 1495, 1420, 1210, 1130, 790, 740, 700 cm^{-1}; ^{1}H NMR δ 7.63 (d, 2 H, J = 8.7 Hz), 7.46 (d, 2 H, J = 8.1 Hz), 7.33 (d, 2 H, J = 8.7 Hz), 7.27 (d, 2 H, J = 8.1 Hz), 2.41 (s, 3 H) ppm; ^{13}C NMR δ 148.73, 141.64, 137.99, 136.40, 129.70, 128.62, 127.01, 121.55, 118.80 (q, J = 320.7 Hz), 21.10 ppm; EIMS *m/e* 316 (M$^+$, 47), 184 (14), 183 (100), 155 (27), 153 (9), 152 (8), 128 (9), 69 (10); HRMS calcd for $C_{14}H_{11}O_5SF_3$ 316.03809, found 316.0364.

Acknowledgment. Financial support by the DGICYT (Project MAT 91-0032) is gratefully acknowledged. One of us (G.M.) thanks the Ministry of Education (Spain) for a predoctoral fellowship. We also like to thank Prof. A. Echavarren and A. García Raso for helpful discussions during the course of this work, as well as for a sample of stannane **3a** (A.E.).

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for compounds **5d**, **6b**, **6e**, **9**, **10**, **11a**, and **11c** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.