Palladium-Catalyzed Cross-Coupling Reactions of Dry Arenediazonium *o*-Benzenedisulfonimides with Aryltin Compounds

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Abstract: The palladium-catalyzed cross-coupling reaction between various arenediazonium *o*-benzenedisulfonimides and aryltin derivatives is described. The procedure is general, easy and gives pure biaryls in good yields (25 examples, average yield 79%). *o*-Benzenedisulfonimide can be recovered (>80%) and reused to prepare again the starting material.

Key words: palladium, Stille reaction, cross-coupling, diazonium compounds, sulfur

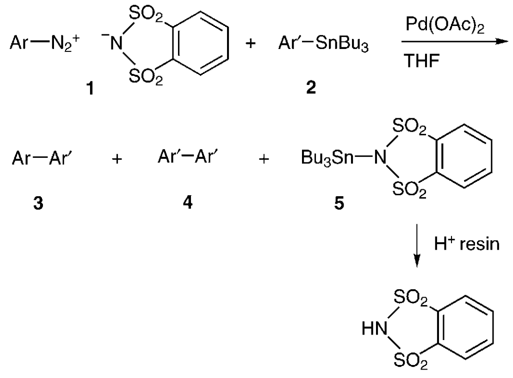
Transition metal-catalyzed cross-coupling reactions of organometallic compounds with organic electrophiles represent one of the most powerful methods for the construction of C–C bonds.[1]

In recent years, the palladium-catalyzed cross-coupling reaction has evolved as a powerful synthetic tool for the synthesis of biaryls,[2] which are fundamental building blocks in organic synthesis. The biaryl unit is in fact present in several compounds of current interest, as in the case of natural products, polymers, advanced materials, liquid crystals, ligands and molecules of medicinal interest. Thus, their preparation is an important synthetic goal.[3]

The reaction, which is by far superior to the classical biaryl synthesis[4] (Gomberg–Bachmann) usually involves the coupling of an arylmetal compound with an aryl electrophile in the presence of a palladium(0) catalyst. Among all the possible arylmetals[5] used as nucleophilic partners, in particular boronic acids[6] or their derivatives (Suzuki coupling) and organotin compounds[7] (Stille coupling) found widespread synthetic application.

The aryl electrophile component is frequently limited to the use of halides (Br, I) or triflates,[8] although in recent times, diazonium salts[9–11] were also used as electrophiles, particularly in the case of the Suzuki reaction.[9] Biaryls are usually obtained in good yields.

Only few examples are reported concerning the reactions of diazonium salts with organotin compounds.[10] Particularly, only two instances are reported in regard to diazonium salt arylation in a Stille coupling.[11] The most significant one,[11a] the coupling reaction of 4-toluenediazonium tetrafluoroborate with tributylphenyltin in the presence of palladium(II)acetate or palladium(0)DBA as catalysts in acetonitrile under nitrogen atmosphere, mainly affords the cross-coupling product, beside the homocoupling products. The highest yield obtained in a cross-coupling reaction (4-methylbiphenyl) was 66% beside 7% of biphenyl and 3% of the homo-coupling product, 4,4′-dimethylbiphenyl.



Ar in **1**,**3**	Ar in **1**,**3**	Ar′ in **2**,**3**,**4**
a 2-MeC_6H_4	**i** 2-$NO_2C_6H_4$	**a** C_6H_5
b 3-MeC_6H_4	**j** 3-$NO_2C_6H_4$	**b** 4-$MeOC_6H_4$
c 4-MeC_6H_4	**k** 4-$NO_2C_6H_4$	**c** 4-ClC_6H_4
d 2-$MeOC_6H_4$	**l** 4-$MeCOOC_6H_4$	**d** 2,6-$(Me)_2C_6H_3$
e 3-$MeOC_6H_4$	**m** 4-CNC_6H_4	**e** 2-Furyl
f 4-$MeOC_6H_4$	**n** 2,6-$(Me)_2C_6H_3$	**f** 2-Thienyl
g 4-BrC_6H_4	**o** 2,6-$(NO_2)_2C_6H_3$	
h 4-IC_6H_4		

Scheme 1

My recent research resulted in a new and large family of anhydrous diazonium salts, the arenediazonium *o*-benzenedisulfonimides **1**.[12] Due to their properties, they have great potential for numerous synthetic applications. These salts are in fact easy to prepare and isolate, extremely stable, and they can be stored for unlimited time. These salts react easily in water but also in organic solvents and, when the reaction has come to an end, an easy recovery and reuse of *o*-benzenedisulfonimide **6** is possible.

On continuing studies dealing with synthetic potential development of the dry arenediazonium *o*-benzenedisulfonimides, this paper describes an improved and general procedure concerning the preparation of biaryls **3** by palladium-catalyzed reaction of dry arenediazonium *o*-benzenedisulfonimides **1** with aryltin derivatives **2** (Scheme 1). The adopted model was the above cited synthesis of biaryls using arenediazonium tetrafluoroborates and aryltin compounds.[11a]

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To begin with, 4-toluenediazonium *o*-benzenedisulfonimide (**1c**) was reacted with tributylphenyltin (**2a**) at room temperature in the presence of a catalytic amount (5%) of palladium(II) acetate and different solvents were tested. The results are listed in Table 1. Using acetonitrile as solvent, besides the cross-coupling product 4-methylbiphenyl (**3c**), the presence of the homo-coupling products 4,4′-dimethylbiphenyl and biphenyl (**4a**) was observed (entry 1). Using methanol as solvent, the yield of 4-methylbiphenyl (**3c**) was very poor because the main reaction was the reduction of the diazonium salt **1c** with the formation of toluene (entry 2). In entries 3 and 4 it is shown that, using ethereal solvents such as 1,4-dioxane or THF, good results were possible. In particular, in the case of tetrahydrofuran, only the cross-coupling product, 4-methylbiphenyl (**3c**) was obtained. No traces of the possible homo-coupling product 4,4′-dimethylbiphenyl were detected.

The same reactions were also carried out using 4-toluenediazonium tetrafluoroborate, but the yields of the product **3c** were lower (Table 1).

Table 1 Trial Reactions

Entry	Solvent	Time (min)	Yield (%)[a,b] 3c	4a	By-product[c]
1	MeCN	180	46 (25)	17 (15)	18 (9)
2	MeOH	10	16 (7)	35 (32)	tr[d,e] (–)
3	1,4-Dioxane	120	76 (49)	12 (12)	9 (6)
4	THF	90	95 (65)	3 (8)	– (–)

[a] Yields refer to the pure products isolated by column chromatography.

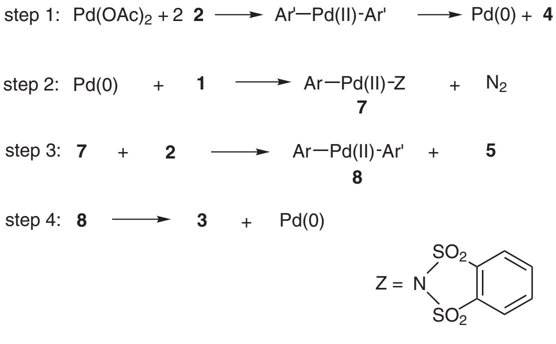
[b] Yields in brackets refer to the reactions carried out with 4-toluenediazonium tetrafluoroborate.

[c] Yields refer to 4,4′-dimethylbiphenyl.

[d] tr = traces.

[e] Presence of toluene, MS (EI, 70 eV): *m*/*z* (%) = 92 (100) [M$^+$] was detected on MS analyses but was not recovered owing to its volatility.

The cross-coupling reaction between anhydrous arenediazonium *o*-benzenedisulfonimides **1** and aryltin derivatives **2** can be described in four steps (Scheme 2): 1) formation of palladium(0); 2) oxidative addition; 3) transmetallation, and 4) reductive elimination.[7b,9b,11a] The palladium(0) catalyst (step 1) formed by reduction of palladium(II)acetate with aryltin derivatives **2**, via transmetallation followed by reductive elimination; afterwards palladium(0) participates in the catalytic cycle promoting the oxidative addition with arenediazonium *o*-benzenedisulfonimide **1** (step 2). The next steps are the transmetallation reaction of the intermediate **7** with aryltin derivative **2** (step 3) and the reductive elimination (step 4) with palladium(0) regeneration and the formation of biaryls **3**.



Scheme 2

On these grounds, the reactions of different dry arenediazonium *o*-benzenedisulfonimides **1** with various aryltin derivatives **2** were tested. All the reactions were carried out in THF in the presence of 5% of palladium(II) acetate at room temperature or 40 °C. The results are listed in Table 2. Biaryls **3a**–**x** were obtained in high yields (average yield 79%) either from diazonium salts bearing electron-donating groups or from salts bearing electron-withdrawing groups. In the presence of *ortho*-substituted arenediazonium *o*-benzenedisulfonimides **1a**, **1d**, and **1i** (Table 2, entries 1, 4, and 8) it was necessary to heat the reaction mixture to 40 °C, but it was possible to recover biaryls **3a**, **3d**, and **3h** in good yields.

On the contrary, reacting sterically hindered diazonium salts **1n** and **1o** with tributylphenyltin (**2a**) and tributyl(4-methoxyphenyl)tin (**2b**) respectively, compounds **3m** and **3p** were obtained in limited amount (Table 2, entries 13 and 16).

Table 2 Biaryls **3**

Entry	Biaryl **3**	Ar	Ar′	Temp (°C)	Time (min)	Chromatographic solvent[a]	Yield[b] (%) 3	4	Biaryls **3** MS *m*/*z* (%) [M$^+$]	mp[c] or bp (°C/torr)	lit. mp or bp (°C/torr)
1	**3a**	2-MeC$_6$H$_4$	C$_6$H$_5$	40	90	PE	89	6	168 (100)	123/0.5	130–136/27[13]
2	**3b**	3-MeC$_6$H$_4$	C$_6$H$_5$	r.t.	90	PE	88	6	168 (100)	131/0.5	148–150/20[13]
3	**3c**	4-MeC$_6$H$_4$	C$_6$H$_5$	r.t.	90	PE	95	3	168 (100)	47–48	46–47[14]

Table 2 Biaryls **3** (continued)

Entry	Biaryl **3**	Ar	Ar′	Temp (°C)	Time (min)	Chromatographic solvent[a]	Yield[b] (%)		Biaryls **3**		
							3	**4**	MS *m*/*z* (%) [M$^+$]	mp[c] or bp (°C/torr)	lit. mp or bp (°C/torr)
4	**3d**	2-$MeOC_6H_4$	C_6H_5	40	90	PE	81	6	184 (76)	31–32	29[15]
5	**3e**	4-$MeOC_6H_4$	C_6H_5	r.t.	120	PE–EE (9.8: 0.2)	90	9	184 (88)	88–89	89[15]
6	**3f**	4-BrC_6H_4	C_6H_5	r.t.	60	PE	90	3	232 (98)	91–92	90[15]
7	**3g**	4-IC_6H_4	C_6H_5	r.t.	30	PE	90	6	280 (67)	110–111	112–113[9b]
8	**3h**	2-$NO_2C_6H_4$	C_6H_5	40	120	PE–EE (9.8: 0.2)	90	9	199 (100)	38–39	37[15]
9	**3i**	3-$NO_2C_6H_4$	C_6H_5	r.t.	90	PE–EE (9.8: 0.2)	90	9	199 (100)	59–60	59[15]
10	**3j**	4-$NO_2C_6H_4$	C_6H_5	r.t.	150	PE–EE (9.8: 0.2)	90	6	199 (100)	115–116	113[15]
11	**3k**	4-$MeCOOC_6H_4$	C_6H_5	r.t.	60	PE–EE (9.8: 0.2)	81	9[d]	212 (56)	116–117	115–116[14]
12	**3l**	4-CNC_6H_4	C_6H_5	r.t.	30	PE–EE (9.8: 0.2)	82	6	179 (100)	87–88	82–84[16]
13	**3m**	2,6-$(NO_2)_2C_6H_3$	C_6H_5	40	90	PE	23	33[e]	244 (100)	190–191	189–191[17]
14	**3n**	3-$MeOC_6H_4$	4-$NO_2C_6H_4$[f]	r.t.	90	PE–EE (9:1)	85	tr[g]	229 (77)	91–92	90–91[18]
15	**3o**	3-$NO_2C_6H_4$	4-$MeOC_6H_4$	r.t.	60	PE–EE (9:1)	83	6	229 (81)	173–174	174–175[19]
16	**3p**	2,6-$Me_2C_6H_3$	4-$MeOC_6H_4$	40	8 h	PE	22	30[h]	212 (65)	52–53	50–51[20]
17	**3p**	4-$MeOC_6H_4$	2,6-$Me_2C_6H_3$	40	24 h	PE	73	–	212 (65)	52–53	50–51[20]
18	**3q**	4-$NO_2C_6H_4$	2,6-$Me_2C_6H_3$	40	10 h	PE	78	–	227 (45)	122–123	[i]
19	**3r**	2-MeC_6H_4	2,6-$Me_2C_6H_3$	40	24 h	PE	70	–	196 (49)	98–99/0.8	117/3[21]
20	**3s**	4-$MeOC_6H_4$	4-ClC_6H_4	r.t.	105	PE	87	tr[g]	218 (87)	110–111	110–111[22]
21	**3t**	4-$NO_2C_6H_4$	4-ClC_6H_4	r.t.	90	PE–EE (9.8: 0.2)	88	tr[g]	233 (86)	146–147	144–145[16]
22	**3u**	4-MeC_6H_4	2-furyl	r.t.	120	PE	76	tr[g]	158 (37)	67–68/0.8	57–58/0.5[23]
23	**3v**	4-$NO_2C_6H_4$	2-furyl	r.t.	120	PE	61	tr[g]	189 (56)	124–125	122–124[24]
24	**3w**	4-MeC_6H_4	2-thienyl	r.t.	90	PE	78	tr[g]	174 (45)	63–64	60–61[25]
25	**3x**	4-CNC_6H_4	2-thienyl	r.t.	90	PE	84	tr[g,j]	185 (46)	186–187	184–185[26]

[a] PE = petroleum ether; EE = diethyl ether.

[b] Yields refer to the pure products isolated by column chromatography.

[c] Crystallization solvent: MeOH.

[d] Traces of methyl benzoate {MS (EI, 70 eV): *m*/*z* (%) = 136 (70) [M$^+$]} were also recovered.

[e] 1,3-Dinitrobenzene (1.05 g, 34%) {MS (EI, 70 eV): *m*/*z* (%) = 168 (87) [M$^+$]} was also recovered.

[f] Trimethyl(4-nitrophenyl)tin was used.

[g] tr = traces.

[h] Presence of 1,3-xylene {MS (EI, 70 eV): *m*/*z* (%) = 106 (87) [M$^+$]} was detected on MS analyses but was not recovered owing to its volatility.

[i] 2,6-Dimethyl-4′-nitrobiphenyl **3q** is known,[27] but physical and spectral data are not reported. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.02$ (s, 6 H, 2 CH_3), 7.11–7.24 (m, 3 H_{arom}), 7.35 and 8.31 (2 d, 1:1, $J = 8.8$ Hz, 4 H_{arom}). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.8$, 124.5, 126.9, 127.8, 128.5, 136.8, 138.0, 142.9, 147.1.

[j] Traces of benzonitrile {MS (EI, 70 eV): *m*/*z* (%) = 103 (100) [M$^+$]} were also recovered.

It is reported that the reactions between arenediazonium tetrafluoroborate and arylboronic acids are limited to sterically unhindered arylboronic acids.[9] On the contrary, here it was found that, with the hindered aryltin derivative tributyl(2,6-dimethylphenyl)tin (**2d**), it was possible to recover the biaryl derivatives in good yields, as reported in the literature regarding the Stille cross-coupling of aryl chlorides.[7g] Therefore, compounds **3p**–**3r** were obtained in good yields when tributyl(2,6-dimethylphenyl)tin (**2d**) reacted with salts **1f, 1k and 1a** respectively (Table 2, entries 17–19).

It must be stressed that this reaction is chemoselective; in fact, no traces of terphenyl were detected in the reaction of diazonium salts **1g** and **1h** (Table 2; entries 6 and 7) bearing a halogen atom that potentially could react as a diazonium group.

It was always possible to recover a large amount of *o*-benzenedisulfonimide (**6**) (average yield of compound **6** recovery was 83%), which was reusable for the preparation of salts **1**.

In conclusion, the importance and the synthetic utility of the coupling reaction with dry arenediazonium *o*-benzenedisulfonimides and aryltin compounds as a powerful method for the formation of biaryls is largely due to the mildness of the reaction, to the easy synthesis of aryltin compounds and arenediazonium *o*-benzenedisulfonimides, to the high yields and to the cleanness of the reactions; there are no side reactions that may complicate isolation and purification of the biaryl.

Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively. Petroleum ether (PE) refers to the fraction boiling in the range 40–70 °C. ^{1}H NMR spectra were recorded on a Brucker Avance 200 spectrometer. Mass spectra were recorded on an HP 5989B mass selective detector connected to an HP 5890 GC cross-linked methyl silicone capillary column. Room temperature (r.t.) is 20–25 °C. Chromatographic solvent, yields and physical and spectral data (MS) of the pure (GC, GC-MS, TLC, ^{1}H NMR) isolated biaryls **3a**–**x** are reported in Table 2. Structures of all the products obtained in this research were confirmed by comparison of their physical (mp or bp) and spectral data with those reported in the literature.

Tributyltin chloride, tributylphenyltin, 2-(tributylstannyl)furan, 2-(tributylstannyl)thiophene, palladium(II) acetate were purchased from Aldrich; Dowex 50X8 ion-exchange resin was purchased from Fluka.

Tributylaryltins 2; General procedure[28]

The suitable Grignard reagent (12 mmol) was added dropwise to a solution of tributyltin chloride (3.25 g, 10.0 mmol) in anhyd Et_2O (35 mL). The resultant solution was heated gently at reflux for 2 h. The reaction mixture was poured into Et_2O–sat. aq NaCl soln (200 mL, 1:1). The organic phase was separated, washed with H_2O (2 × 100 mL), dried (Na_2SO_4) and evaporated under reduced pressure. The crude residue was distilled to provide the pure title compounds. Yields, physical and spectroscopic properties of the title compounds are given below.

Tributyl(4-methoxyphenyl)tin (2b)

Yield: 3.70 g (93%); bp 171 °C/1 mmHg; tributyl(4-methoxyphenyl)tin is known in the literature,[29] but physical and spectral data are not reported.

MS (EI, 70 eV): *m/z* (%) = 341 (45) [$M^+ - Bu$].

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 7.5$ Hz, 9 H, 3 CH_3), 0.99–1.08 (m, 6 H, 3 CH_2), 1.24–1.43 (m, 6 H, 3 CH_2), 1.47–1.59 (m, 6 H, 3 CH_2), 3.95 (s, 3 H, OCH_3), 6.91 and 7.38 (2 d, 1:1, $J = 8.5$ Hz, 4 H_{arom}).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.6$, 13.8, 27.1, 29.0, 56.4, 113.2, 134.8, 136.9, 161.9.

Tributyl(4-chlorophenyl)tin (2c)

Yield: 3.56 g (89%); bp 157 °C/0.8 mmHg (lit.[30] bp 138 °C/0.02 mmHg).

MS (EI, 70 eV): *m/z* (%) = 345 (52) [$M^+ - Bu$].

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.5$ Hz, 9 H, 3 CH_3), 0.95–1.03 (m, 6 H, 3 CH_2), 1.21–1.36 (m, 6 H, 3 CH_2), 1.41–1.52 (m, 6 H, 3 CH_2), 7.23 and 7.32 (2 d, 1:1, $J = 9.1$ Hz, 4 H_{arom}).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.8$, 14.2, 27.9, 30.1, 128.9, 133.9, 138.3, 141.1.

Tributyl(2,6-dimethylphenyl)tin (2d)

Yield: 1.57 g (40%); bp 193 °C/18 mmHg.

MS (EI, 70 eV): *m/z* (%) = 339 (22) [$M^+ - Bu$].

^{1}H NMR ($CDCl_3$): $\delta = 0.83$ (t, $J = 7.5$ Hz, 9 H, 3 CH_3), 0.93–1.04 (m, 6 H, 3 CH_2), 1.21–1.36 (m, 6 H, 3 CH_2), 1.41–1.52 (m, 6 H, 3 CH_2), 2.46 (s, 6 H, 2 CH_3), 7.07–7.09 (m, 3 H_{arom}).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 12.2$, 13.8, 19.8, 27.8, 29.5, 125.4, 126.2, 144.1, 145.5.

Anal. Calcd for $C_{20}H_{36}Sn$: C, 60.79; H, 9.18; Sn, 30.03. Found: C, 60.69; H, 9.21; Sn, 30.10.

Trimethyl(4-nitrophenyl)tin was prepared according to the procedure reported in the literature.[31]

Dry arenediazonium *o*-benzenedisulfonimides **1a**–**o** were prepared as described previously by us.[12] The crude salts were virtually pure and were used without further crystallization.

2,6-Dinitrobenzenediazonium *o*-Benzenedisulfonimide (1o)

Yield: 89%; dp 181–182 °C (HCO_2H).

^{1}H NMR (200 MHz, CF_3CO_2D): $\delta = 8.23$–8.48 (m, 4 H_{arom}), 9.21 (t, $J = 8.3$ Hz, 1 H_{arom}), 9.47–9.50 (m, 2 H_{arom}).

^{13}C NMR (50 MHz, CF_3CO_2D): $\delta = 110.8$, 127.2, 134.7, 130.0, 130.8, 136.9, 149.7.

Anal. Calcd for $C_{12}H_7N_5O_8S_2$: C, 34.87; H, 1.71; N, 16.94; S, 15.51. Found: C, 34.86; H, 1.75; N, 16.90; S, 15.56.

CAUTION! In our laboratory there was no case of sudden decomposition during the preparation, purification and handling of salts **1**. Nevertheless, it must be borne in mind that all diazonium salts in the anhydrous state are potentially explosive. Therefore, they must be carefully stored and handled.

4-Methylbiphenyl (3c); Typical Procedure

4-Toluenediazonium *o*-benzenedisulfonimide (**1c**) (3.37 g, 10.0 mmol) was added in one portion with vigorous stirring to a solution of tributylphenyltin (**2a**) (4.04 g, 11.0 mmol) in THF (30 mL). Then, palladium(II) acetate (0.50 mmol, 0.11 g) was added in one portion. Stirring at r.t. was maintained for 90 min. The completion of the reaction was confirmed by absence of azo-coupling with 2-naphthol. GC,GC-MS, and TLC (PE) analyses of the reaction mixture showed 4-methylbiphenyl (**3c**), MS (EI, 70 eV): *m/z* (%) = 168

(100) [M$^+$] as major product, beside biphenyl (**4a**), MS (EI, 70 eV): *m/z* (%) = 154 (100) [M$^+$] as minor product. Furthermore, GC-MS analysis showed the presence of *o*-benzenedisulfonilimidotributyltin (**5**), MS (EI, 70 eV): *m/z* (%) = 420 (15) [M$^+$–Bu]. All attempts to isolate compound **5** failed. The solution was poured into Et_2O–H_2O (200 mL, 1:1), The aqueous layer was separated and extracted with Et_2O (50 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and dried (Na_2SO_4). After solvent removal under reduced pressure, the crude residue was chromatographed on a short column, under pressure, eluting with PE. The first-eluted product was biphenyl (**4a**) (0.03 g, 3% yield); the second-eluted product was the pure (GC, GC-MS, TLC, ^{1}H NMR) title compound **3c** (1.60 g, 95% yield); identical physical and spectral data with commercially available samples of analytical purity (Aldrich) were observed for each product.

The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. The black tarry residue was passed through a column of Dowex 50X8 ion-exchange resin (1.6 g/1 g of product) and with H_2O (about 50 mL) as eluent. After removal of H_2O under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**6**) was recovered (1.90 g, 87% yield); mp 192–194 °C (toluene) (lit.[12] mp 192–194 °C).

Details of the reactions 1–24 and yields of the pure (GC, GC-MS, TLC, ^{1}H NMR) biaryls **3a**–**w**, isolated by column chromatography, are listed in Table 2. The structures of all the products were confirmed by comparison of their physical (mp or bp) and spectral data (^{1}H NMR) with those reported in the literature or with those of the corresponding commercially available samples of analytical purity.

Trial Reactions

All the reactions reported in Table 1 (entries 1–4) were carried out according to the general procedure described above, reacting 4-methylbenzenediazonium *o*-benzenedisulfonimide (**1a**) (3.37 g, 10.0 mmol) with tributylphenyltin (**2a**) (4.04 g, 11.0 mmol) at r.t. in varying solvents. The crude residues were chromatographed on a short column with with PE as eluent. Details are shown in Table 1.

Collateral proofs were carried out under the same conditions, reacting 4-toluenediazonium tetrafluoroborate (2.06 g, 10.0 mmol) (prepared according to the general procedure reported in the literature)[32] with tributylphenyltin (**2a**) (4.04 g, 11.0 mmol). Details are shown in Table 1.

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