Aryl Mesylates in Metal-Catalyzed Homocoupling and Cross-Coupling Reactions. 1. Functional Symmetrical Biaryls from Phenols via Nickel-Catalyzed Homocoupling of Their Mesylates

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Aryl sulfonates including mesylate derived from phenols are converted in high yields to biaryls by homocoupling in the presence of catalytic amounts of zero-valent nickel catalysts generated *in situ*. This reaction provides the most convenient method for the synthesis of many functional symmetrical biaryls and was applied to the preparation of 2,2′-, 3,3′-, and 4,4′-disubstituted biphenyls and other biaryls. The influence of the electronic and steric effects of substituents attached in the ortho, meta, and para positions of aryl sulfonates and the nature of the sulfonate leaving group on the yield of homocoupled product as well as their influence on the extent of various side reactions were investigated. In addition, the influence of the effects of the polarity and dryness of solvent, halide ion source and concentration, and ratio of catalyst and ligand to aryl sulfonate are discussed.

Introduction

Symmetrical biaryls were traditionally obtained by the Ullmann reaction[1] and more recently by Ni(0)-catalyzed homocoupling of aryl halides.[2] The original method for the homocoupling of aryl halides based on stoichiometric amounts of preformed Ni(0) catalysts[2a-c] was first extended to the use of stoichiometric amounts of Ni(0) reagents generated *in situ*[2d] and then adapted to catalytic amounts of Ni(0) species.[2e-g] A Pd-catalyzed desulfonative homocoupling of arylsulfonyl chlorides was recently reported.[3] Unsymmetrical biaryls are synthesized by Pd(0)-catalyzed cross-coupling of aryl halides with arylstannanes,[4] arylboronic acids,[5] arylboronic esters,[6] and arylzinc derivatives.[7] This last reaction can be also carried out in the presence of Ni(0) catalysts.[7] As compared with the classic Ullmann reaction, both the Pd(0)- and Ni(0)-catalyzed coupling reactions proceed under very mild conditions and tolerate a large variety of functional groups.

Recently, it has been shown that aryl triflates behave analogously to enol triflates in a series of Pd(0)-catalyzed cross-coupling reactions.[8] Subsequently, unsymmetrical biaryls were prepared by the Pd(0)-catalyzed cross-coupling of aryl triflates with arylstannanes[9] and arylboronic acids[10a] or esters.[10b] Additional procedures for the synthesis of unsymmetrical biaryls are based on the cross-coupling of aryl triflates with organocopper reagents,[11] on the Pd-catalyzed cross-coupling of arylfluorosilanes with aryl iodides,[12] and of aryl acid chlorides with disilanes.[13] Aryl triflates were also cyanated[14ab] and have been cross-coupled with organocopper[11] and Grignard[15] reagents by Ni(0)-catalyzed reactions. Aryl triflates have undergone catalytic reduction in the presence of Ni(0)[16a] and Pd(0)[16b] catalysts. The palladium-catalyzed carbonylation of aryl triflates was also reported.[17]

The Ni(0)-catalyzed homocoupling of aryl triflates,[18a] aryl tosylates,[18b] and one example of an aryl mesylate[18b] to symmetrical biaryls were first reported to proceed under ultrasonication. A low yield (21%) was reported

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for the coupling reaction of the aryl mesylate.[18b] Subsequently, we have shown that Ni(0)-catalyzed homocoupling of bistriflates takes place in the absence of ultrasonication, and this reaction yielded a convenient method for the synthesis of functional poly(*p*-phenylene)s and polyarylenes.[18c-e] Pd-catalyzed electrosynthesis of biaryls from aryl triflates was also reported.[18g] Recently, while the work reported in the present paper was in progress, a communication reported the Ni(0)- and Pd(0)-catalyzed homocoupling of aryl triflates[18f] and a patent reported the Ni(0)-mediated homocoupling of aryl sulfonates including one example of an aryl mesylate.[18h]

Therefore, alternative sulfonate leaving groups on aromatic substrates besides triflates were only briefly investigated in Ni(0)- and Pd(0)-mediated reactions.[19] Aryl mesylates and tosylates have been generally considered to have a poor reactivity toward transition metal catalysts, and only a few experiments have indicated the contrary. For example, reports have been made of the Pd(0) catalyzed reduction of aryl mesylate,[20] the $NaBH_4$–$NiCl_2$-mediated reduction of aryl tosylate,[21] and the cobalt-catalyzed methoxycarbonylation of aryl tosylate.[22] Two publications have mentioned the Pd(0)-catalyzed cross-coupling of aryl fluorosulfonates,[23a] aryl *p*-fluorophenylsulfonates,[23b] and a few other sulfonates with arylstannanes[23b] and two very brief experiments on the Ni(0)-catalyzed homocoupling of 1-naphthyl tosylate.[18f]

The use of aryl sulfonates in Ni(0)- and Pd(0)-catalyzed reactions are of interest since they provide access to biaryls starting from phenols. Recently, we became interested in the evaluation of less expensive leaving groups than triflates for the transformation of phenols into symmetrical and unsymmetrical biaryls via various Ni(0)- and Pd(0)-catalyzed homocoupling and cross-coupling reactions. The goal of the paper is to report our results which demonstrate that the most common aryl sulfonates including aryl mesylates undergo Ni(0)-catalyzed homocoupling reactions under mild conditions resulting in high yields of symmetrical biaryls. An investigation of the scope of this reaction using varying reaction conditions was undertaken. The application of this synthetic method to the facile preparation of well-known functional biaryls from readily available phenols will be demonstrated. Because substituted phenols, hydroquinones, and bisphenols are readily available and inexpensive, the use of the mesylate leaving group in Ni(0)-catalyzed homocoupling reactions provides the most convenient access to already known and to new functionalized symmetrical biaryls.

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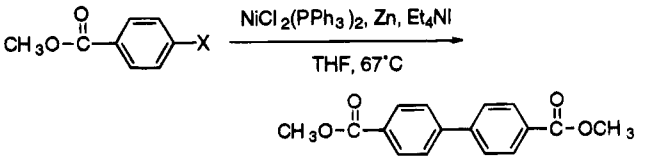
Table 1. Ni(0)-Catalyzed Homocoupling of Various *p*-Carbomethoxyphenyl Sulfonates[a]

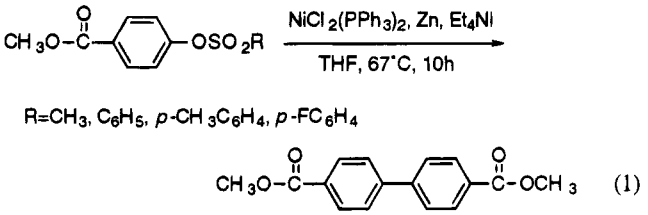


entry	leaving group X	reaction time (h)	GC yield[b] (%)
1	CF_3SO_2O	5	>99
2	*p*-$FPhSO_2O$	5	>99 (85)
3	*p*-$ClPhSO_2O$	10	(79)[c]
4	$PhSO_2O$	5	97 (83)
5	*p*-CH_3PhSO_2O	10	>99
6	CH_3SO_2O	10	>99

[a] Reaction conditions: 10 mol % of $NiCl_2(PPh_3)_2$, 1.7 equiv of Zn, 1.5 equiv of Et_4NI, refluxing THF, N_2. [b] Isolated yields in parentheses. [c] Chlorine of 4-chlorobenzenesulfonate moiety was also homocoupled and cross-coupled to give complicated byproducts.

Results and Discussion

Effects of Substituents and Leaving Groups on the Synthesis of 2,2′-, 3,3′-, and 4,4′-Disubstituted Biphenyls and Biaryls. The homocoupling reactions of aryl sulfonates were mediated by a nickel catalyst generated from $NiCl_2(PPh_3)_2$ (0.10 equiv) in the presence of excess Zn (1.7 equiv) and Et_4NI (1.5 equiv) in THF (eq 1).

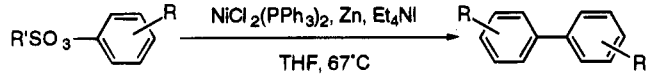


This method of generating the Ni(0) catalyst *in situ* was first developed for the homocoupling of aryl halides in THF (*vide infra*).[2g] The reaction is regiospecific with no isomerization detected.

A series of the nickel-catalyzed homocoupling reactions was performed with various *p*-carbomethoxyphenyl sulfonates, in order to evaluate the effectiveness of sulfonate leaving groups which could be used in place of triflate (Table 1). The use of three sulfonate leaving groups, *p*-toluenesulfonate, *p*-fluorobenzenesulfonate, and methanesulfonate, resulted in high yields (>99%) equal to those obtained with the triflate (entries 1, 2, 5, and 6). The reactivity of the *p*-fluorobenzenesulfonate leaving group was similar to that of the triflate, as the reaction times were identical. The reaction time was doubled (10 h) when using the *p*-toluenesulfonate or methanesulfonate leaving groups. A slightly reduced yield (97%) was obtained after 5 h for the benzenesulfonate leaving group. A decreased yield (79% isolated) was obtained with the 4-chlorobenzenesulfonate leaving group. In this case the reduced yield was at least partly due to the participation of the chloro group as a leaving group in the coupling reaction.

The effect of various substituents on the coupling reaction when using benzenesulfonate or *p*-fluorobenzenesulfonate leaving groups was studied (Table 2). High yields were obtained when benzenesulfonate was the

Table 2. Effect of Various Substituents on the Ni(0)-Catalyzed Homocoupling of Aryl Sulfonates[a]



entry	R	R'	reaction time (h)	GC yield[b] (%)
1	*p*-CO_2CH_3	Ph	5	97 (83)
2	*p*-CH_3	Ph	5	67 (48)
3	*p*-CH_3	Ph	10	90
4	*p*-OCH_3	Ph	10	94
5	*p*-$COCH_3$	*p*-FPh	5	98[c]
6	*p*-CO_2CH_3	*p*-FPh	5	>99 (85)
7	*o*-CO_2CH_3	*p*-FPh	24	>99
8	*p*-Ph	*p*-FPh	5	>99[d]
9	H	*p*-FPh	5	>99
10	*p*-CH_3	*p*-FPh	5	93 (80)
11	*o*-CH_3	*p*-FPh	5	72
12	*p*-OCH_3	*p*-FPh	5	85 (71)

[a] Reaction conditions are identical to those in Table 1. [b] Isolated yields in parentheses; trace amounts of transarylation byproducts were found in most experiments. [c] 2% of 4-acetylbiphenyl was detected. [d] Actual yield based on the disappearance of the substrate. The product was insoluble.

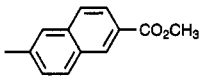
leaving group (entries 1–4). The *p*-carbomethoxy-substituted aryl benzenesulfonate was substantially more reactive than both the *p*-methyl- and *p*-methoxy-substituted aryl benzenesulfonates. A doubling of the reaction time was necessary in the latter two cases. The *p*-fluorobenzenesulfonate leaving group gave higher yields than the benzenesulfonate group when identical reaction times were used (entries 1 and 6 and entries 2 and 10). The ortho-substituted substrates reacted more sluggishly than the para-substituted substrates. This is reflected in the reduced yield obtained for *o*-methyl (entries 10 and 11) and the longer reaction time required for *o*-carbomethoxy (entries 6 and 7). Slightly lower reactivity was obtained when the aryl group had electron-donating substituents (entries 9 and 12). This effect was less pronounced with better leaving groups (entries 2 and 10).

In regard to cost, the most important leaving group investigated was the mesylate group. Good to high coupling yields of a number of aryl mesylates were obtained (Table 3). The reaction tolerates a wide range of functional groups: alkyl, ester, ether, fluoro, ketone, nitrile, and phenyl. No coupled product was detected when the nitro group was present, perhaps due to the generation of nitrosonickel(0) complexes[24] or the reduction of the aryl nitro group.

A general trend was apparent in regard to the electronic properties of the aryl substituents. Increased yields, relative to phenyl methanesulfonate, were obtained when the para substituents were electron-withdrawing groups (entries 1–6). The exception was the nitro group (entry 8), which could not tolerate the reaction conditions. Yields were reduced when the para substituent was an electron-donating group (entries 10–13). A reduced yield was obtained when the substituent was a fluoro group (entry 7). While this group is electron-withdrawing via inductive effects, it is electron-donating by resonance effects. Pentafluorophenyl methanesulfonate did not participate in the reaction to give coupled product (entry 14), instead it induced only a O–S bond cleavage. The general trend in reference to the electronic properties of the aryl substituents is that electron-withdrawing groups activate the aryl mesylate and electron-donating groups deactivate the aryl mesylate toward the Ni(0)-promoted coupling reaction.

Table 3. Effect of Various Substituents on the Ni(0)-Catalyzed Homocoupling of Aryl Methanesulfonates[a]

$$CH_3SO_3Ar \xrightarrow[THF,\ 67\ °C]{NiCl_2(PPh_3)_2,\ Zn,\ Et_4NI} ArAr$$

entry	Ar	reaction time (h)	GC yield[b] (%)
1	*p*-$C_6H_4CO_2CH_3$	10	>99
2	*m*-$C_6H_4CO_2CH_3$	10	93
3	*o*-$C_6H_4CO_2CH_3$	10	83
4	*o*-$C_6H_4CO_2CH_3$	24	>99[c]
5	*p*-$C_6H_4COCH_3$	10	73[d]
6	*p*-C_6H_4CN	10	94[e]
7	*p*-C_6H_4F	10	(54)
8	*p*-$C_6H_4NO_2$	10	0
9	Ph	10	91
10	*p*-C_6H_4Ph	10	(60)
11	*p*-$C_6H_4CH_3$	10	84
12	*p*-$C_6H_4OCH_3$	10	83
13	*p*-$C_6H_4OCH_3$	24	70[c]
14	C_6F_5	10	0[f]
15		10	(91)

[a] Reaction conditions are identical to those in Table 1. [b] Isolated yields in parentheses; trace amounts of transarylation byproducts were found in most experiments. [c] Reaction run with additional 2 equiv of PPh_3 relative to $NiCl_2(PPh_3)_2$. [d] Also produced acetophenone (20%) and 4-acetylbiphenyl (7%). [e] 6% of 4-cyanobiphenyl was detected. [f] The remaining material isolated was a mixture of starting substrate and C_6F_5OH.

The position of the substituent also affects the reaction yield. The highest yield was obtained when a *p*-carbomethoxy substituent was present. The order of reactivity for this group was para > meta > ortho (entries 1–3). When in the para position it can have an electron-withdrawing effect by resonance, thus facilitating the oxidative addition step.[25] When the group is in the ortho position steric effects apparently predominate over the electronic effects of the group. However, the yield was increased by lengthening the reaction time in the presence of extra PPh_3 (entry 4). It is well known that Ni(0)-catalyzed aryl–aryl coupling reactions are impeded by substituents in the ortho position.[26]

The major side reactions in Ni(0)- and Pd(0)-catalyzed reactions involving aryl halides and aryl triflates are as follows: reduction,[2a–c,f] transarylation,[2d,f] and phosphonium salt formation.[27] Side reactions were more evident in cases involving the less reactive aryl sulfonates (Table 2, entry 5, vs Table 3, entry 5). Trace amounts of transarylation byproducts were detected in most experiments. These products were formed by the coupling of the aryl mesylate with a phenyl group from PPh_3. Phenyl group transfer from PPh_3 is a common side reaction in Pd- and Ni-catalyzed reactions in the presence of PPh_3.[2f] The phenyl group transfer from PPh_3 was further indicated by the detection of trace amounts of biphenyl when the reaction was performed under identical reaction conditions except for the absence of aryl mesylate substrate. The other side reaction identified was the reduction of the aryl sulfonate. In other coupling reactions two general pathways for aryl reduction have been identified: (a) a reductive elimination process, involving a nickel hydride species, prior to completion of the reaction

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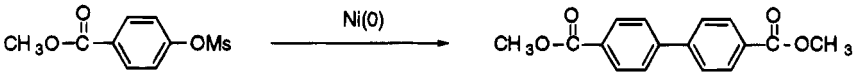
Table 4. Effect of Various Reaction Conditions on the Ni(0)-Catalyzed Homocoupling of Methyl 4-((Methylsulfonyl)oxy)benzoate[a]

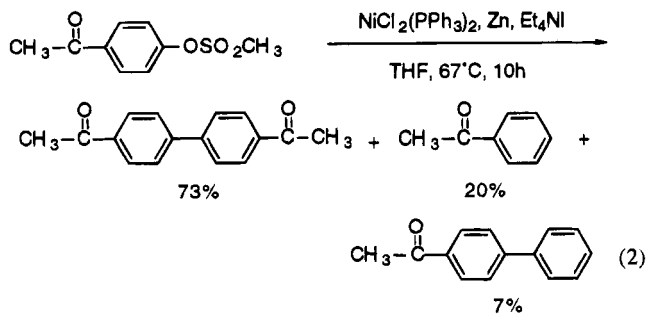


[Ar-OMs] [Ar-Ar]

	reaction condns				GC yield (%)			
entry	$NiCl_2(PPh_3)_2$ (mol %)	PPh_3 (mol %)	halide (equiv)	solvent	ArH	ArOMs	ArPh	ArAr
1	10		Et_4NI/1.5	THF			traces	>99
2	10		Et_4Ni/1.5	DMAc	20	0	2	72[b]
3	10	30	Et_4NI/1.5	DMAc	22	2	1	73
4	10	60	Et_4NI/1.5	DMAc	19	11		60
5	10	60	Et_4NI/1.5	DMAc	15		6	47
6	10		Et_4NI/0.8	THF	6	3	3	87
7	10			THF		29	2	64[b]
8	5		Et_4NI/1.5	THF	3	24	1	69[b]
9	3		Et_4NI/1.5	THF	3	43	traces	53[b]
10	5	20	Et_4NI/1.5	THF	6	7	3	82
11	3	20	Et_4NI/1.5	THF	9	20	1	68
12	1	20	Et_4NI/1.5	THF	9	48	traces	36
13	10		Et_4NBr/1.5	THF	4	15	3	68
14	10		KI/1.5	THF	4	24	traces	67
15[c]	10		KI/1.5	THF	4	traces	2	93
16[c]	10		KBr/1.5	THF	3		4	86
17	10	20		THF	2	2	3	91
18	10	20		THF[d]	3	2	4	90
19	10	10		THF[d]		90		6[b]
20	10	10	Et_4NI/1.5	THF[d]	traces	60		28[b]
21	10			THF[d]		100		
22	10		Et_4NI/1.5	THF[d]		100		
23[e]	10	20		THF	7	4	3	83
24	10	30		THF[d]	3	4	3	90
25[f]	10			THF[d]	2	7	6	83
26[g]	10			THF[d]	10	9	9	55
27	10			pyridine	14	25	traces	55
28	10			THT[h]		100		
29[i]	10			pyridine	14	66		12
30[i]	10			THT[h]		100		
31[i,j]	10			THF[d]		100		
32[k]	5.3	20	NaBr/1.0	DMAc	5		2	78
33[k]	5.3	20	KBr/1.0	DMAc	4		2	79

[a] Reaction conditions: 1.7 equiv of Zn, reaction temperature 67 °C (except reaction temperature in DMAc was 100 °C), and reaction time 10 h unless otherwise noted. [b] Catalyst decomposed in the early stage of the reaction. [c] 20 mol % of 18-crown-6 (based on substrate) was added to the reaction mixture. [d] Wet THF. [e] 5 mol % of H_2O (based on substrate) was added. [f] 20 mol % of pyridine (based on substrate) was added. [g] 20 mol % of tetrahydrothiophene (based on substrate) was added. [h] Tetrahydrothiophene. [i] $NiCl_2$ instead of $NiCl_2(PPh_3)_2$ was employed. [j] 20 mol % of 2,2′-dipyridyl (based on substrate) instead of PPh_3 was employed. [k] 1.0 equiv of Zn, reaction time 3 h.

steps which lead to the coupled product (*vide infra*) and (b) hydrogenolysis via the formation of an aryl radical.[28] Aryl radicals readily abstract hydrogen from THF, enolizable ketones when available, or adventitious protic sources such as water.[2f] For example, in addition to the formation of 73% homocoupled product, the reaction of 4-acetylphenyl methanesulfonate resulted in 20% reduction to acetophenone and 7% transarylation yielding 4-acetylbiphenyl (eq 2). Shorter reaction times decreased



(2)

these side reactions, but also reduced the yield of the homocoupled product. This fairly large amount of reduction product might be rationalized by the lower reduction potential of the aryl mesylate due to the strong electron-withdrawing group. However, for more reactive aryl sulfonates (i.e., aryl *p*-fluorobenzenesulfonates), the reduction product was negligible (Table 2, entry 5).

Solvent Effect. The generation of Ni(0) catalyst *in situ*, from the reduction of $NiCl_2(PPh_3)_2$ with Zn, was used for the homocoupling of aryl halides in both dipolar aprotic solvents such as DMF or DMAc and in less polar solvents such as THF.[2d-g] However, THF was the best solvent in reference to the rate and selectivity of the homocoupling under our reaction conditions which employed coordinatively unsaturated Ni catalyst (i.e., $NiCl_2(PPh_3)_2$, Zn, and Et_4NI) (Table 4, entry 1). Typical dipolar aprotic solvents for Ni(0) homocoupling such as DMAc, which can increase the nucleophilicity of Ni(0) and also act as a donor ligand, gave lower yields under the same reaction conditions (entry 1 vs 2). When DMAc was utilized, a significant amount of most probably colloidal nickel-black deposition occurred within minutes of initiation. Also, a significant amount of reduction side product (20%) was detected. Early catalyst decomposition in DMAc was avoided by increasing the amount of PPh_3.

(28) (a) Tsou, T. T.; Kochi, J. K. *J. Am Chem Soc.* **1979**, *101*, 7547. (b) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

However, this retarded the reaction as relatively low yields and recovered starting material were obtained (entries 3 and 4). An attempt to circumvent the reduced reactivity, in the presence of excess PPh_3, by increasing the reaction temperature (100 °C), resulted in lower yields (entry 4 vs 5). When using THF, no additional PPh_3 was required in the presence of halide source such as Et_4NI (entry 1). Therefore, the *in situ* generated $Ni(0)(PPh_3)_2$ complexes were less stable in more polar and strongly dissociating solvents such as DMAc.

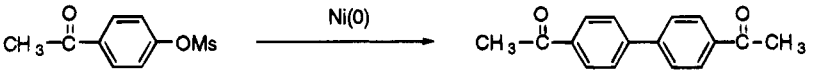
Halide Ion Effect. It is known that halide ions, especially iodide, enhance the reaction rate of nickel-catalyzed homocoupling reactions, although the exact role of halide is somewhat unclear.[2d-g] One role of halide is to function as a bridging ion between nickel and zinc in the electron transfer process.[2e] Under our typical reaction conditions which employ THF as solvent in the absence of additional PPh_3, the coupling reaction proceeded very efficiently in the presence of Et_4NI. Relatively large amounts of Et_4NI (1.5 equiv based on mesylate) were necessary in order to obtain high yields (in the absence of additional PPh_3). An increase in yield occurred as the relative amount of Et_4NI was increased (entries 1, 6, and 7). In the absence of both additional PPh_3 and Et_4NI (entry 7), premature catalyst decomposition resulted in low yield. However, addition of Et_4NI to the reaction significantly enhanced the stability of the Ni(0) catalyst. This may indicate that iodide can act as a donor ligand which can stabilize the Ni(0) catalyst as well as facilitate the electron transfer process. It is important to note that Ni(0) PPh_3 complexes exist in solution entirely as the tris complex, i.e., $Ni(0)(PPh_3)_3$, in the presence of excess PPh_3 due to the bulkiness of the PPh_3 ligand.[2e] However, in the absence of added PPh_3, our catalyst system generates $Ni(0)(PPh_3)_2$. This highly coordinatively unsaturated Ni(0) complex might be stabilized by iodide coordination. Thus, iodide is essential for high yield in the absence of additional PPh_3. However, it was found that in the presence of additional PPh_3, the coupling reaction proceeded efficiently without iodide (91% yield, entry 17). This may indicate that an important role of the halide is to stabilize the arylnickel species and/or to prevent the deactivation of the catalyst which would limit the yield. Other halide sources were compared with Et_4NI. When Et_4NBr was employed, lower yield was observed (entry 1 vs 13). The utilization of KI, which has very low solubility in THF, resulted in yields which were similar to that obtained with no iodide present (entry 7 vs 14). The enhancement of the solubility of KI in THF by the addition of a catalytic amount (20 mol %) of 18-crown-6 resulted in high yield (entry 14 vs 15). When KBr instead of KI together with 18-crown-6 was used, a slightly lower yield was obtained (entry 15 vs 16).

Effect of the Amount of Catalyst. Ni(0) catalyst is decomposed by the decoordination of ligand from metal center and by adventitious traces of water in reaction medium. The decomposition of the Ni(0) catalyst accelerates as the temperature is increased. Therefore, it is important to have enough catalyst initially present so that active catalyst is present at the end of the reaction and the last of the mesylate can be coupled. However, too much catalyst may also be harmful (see mechanistic discussion *vide infra*). The yield of homocoupling decreased as the amount of Ni(0) catalyst decreased in the absence of additional PPh_3 (entries 1, 8, and 9). Almost quantitative yield was obtained with 10 mol % of Ni(0) catalyst (entry 1). When 5 and 3 mol % of Ni(0) catalyst (entries 8–9) was used, premature catalyst decomposition was observed and the remaining material isolated was unreacted aryl mesylate. Addition of PPh_3 to the reaction mixture greatly enhanced the stability of the Ni(0) catalyst, resulting in increased yield (entries 8 vs 10 and 9 vs 11). When 1 mol % Ni(0) catalyst in the presence of 20 mol % PPh_3 was used, 36% coupled product was obtained (entry 12).

Dried versus Wet Solvent. It has been generally accepted that water and oxygen in the reaction medium can result in premature decomposition of Ni(0) catalyst.[2] Water can also reduce aryl halides and aryl sulfonates to the corresponding arene in the presence of zero-valent nickel catalyst. For this reason, careful removal of water in the reaction medium has been a critical factor in Ni(0)-mediated reactions. This is also the reason that most Ni(0) coupling reactions require relatively large amounts of ligands such as PPh_3 and/or bidentate ligands such as 2,2′-dipyridyl in order to strongly stabilize the Ni(0) catalyst. It was discussed that in the presence of additional PPh_3 (20 mol %), the coupling reaction proceeded efficiently without iodide (91% yield, entry 17), *vide supra*. Although some reaction rate retardation was expected, the active Ni(0) catalyst lasted for the entire reaction time. The same reaction conditions employing 20 mol % of PPh_3 except using wet THF (i.e., taken directly from a bottle without drying) instead of dried THF (freshly distilled from sodium benzophenone ketyl) gave almost identical results (entry 17 vs 18). However, when the amount of PPh_3 was decreased from 20 to 10 mol %, with wet THF the catalyst decomposed immediately resulting in very low yield (entry 18 vs 19). A slight increase in yield was detected in the presence of Et_4NI (entry 19 vs 20). In the absence of additional PPh_3, wet THF did not give any homocoupled product even in the presence of Et_4NI (entries 21 and 22). Apparently, at least 20 mol % of additional PPh_3 was essential for the high coupling yield when using wet THF. A further increase in yield by using 30 mol % PPh_3 was not obtained (entry 18 vs 24). In order to confirm the efficiency of the coupling reaction in wet THF, H_2O (5 mol % based on aryl mesylate) was added to the reaction mixture in dried THF, with 20 mol % PPh_3 present. This resulted in a slightly decreased yield (83% yield, entry 23). This amount of H_2O was sufficient to deactivate the catalyst in the absence of added PPh_3.

Ligand Effects. Ligands (such as PPh_3) are essential in Ni(0) homocoupling reaction in order to stabilize the *in situ* generated Ni(0) catalyst and aryl nickel species during the entire reaction sequence. The selection of the appropriate ligand can also increase the electron density on low valent transition metals, making the metal more nucleophilic, thus facilitating the oxidative addition step of the catalytic cycle. However, ligands also should have a proper tendency for dissociation from the metal to generate the coordinatively unsaturated species (i.e., generation of a vacant reacting site). It is well established that this dissociation is highly dependent on the polarity of the solvents and the reaction temperature. When THF is replaced with dipolar aprotic solvents such as DMF or DMAc, the ligand dissociation is much more favored. In the absence of added PPh_3 this sometimes results in premature catalyst decomposition and low yields. However, when less dissociating solvents such as THF are used, decoordination of ligand from Ni(0) catalyst and/or arylnickel species is less favored, and for

Table 5. Effect of Various Reaction Conditions on the Ni(O)-Catalyzed Homocoupling of 4-Acetylphenyl Methanesulfonate[a]



[Ar-OMs] [Ar-Ar]

	reaction condns				GC yield (%)			
entry	$NiCl_2(PPh_3)_2$ (mol %)	PPh_3 (mol %)	halide (equiv)	solvent	ArH	ArOMs	ArPh	ArAr
1	5.3	20	NaBr/1.0	DMAc	2		2	96
2	5.3	20	NaBr/1.0	DMAc	3		1	95
3	5.3	20	NaBr/1.0	DMAc	2		3	65
4	5.3	20	NaI/1.0	DMAc	7		1	91
5	5.3	20	KI/1.0	DMAc	6		1	93
6	5.3	20	Et_4NI/1.0	DMAc	5		7	85
7	5.3	20	NaBr/1.0	DMF	21		7	69
8	5.3	20	NaBr/1.0	NMP	2	60		traces
9	5.3	20		DMAc	4	69	5	16
10	5.3	40		DMAc	8		8	55
11	5.3	20	KI/1.0	DMAc[b]	22	60		17
12	5.3	20	NaBr/1.0	DMAc[b]	19	40		40
13[c]	10		Et_4NI/1.5	THF	20		7	73

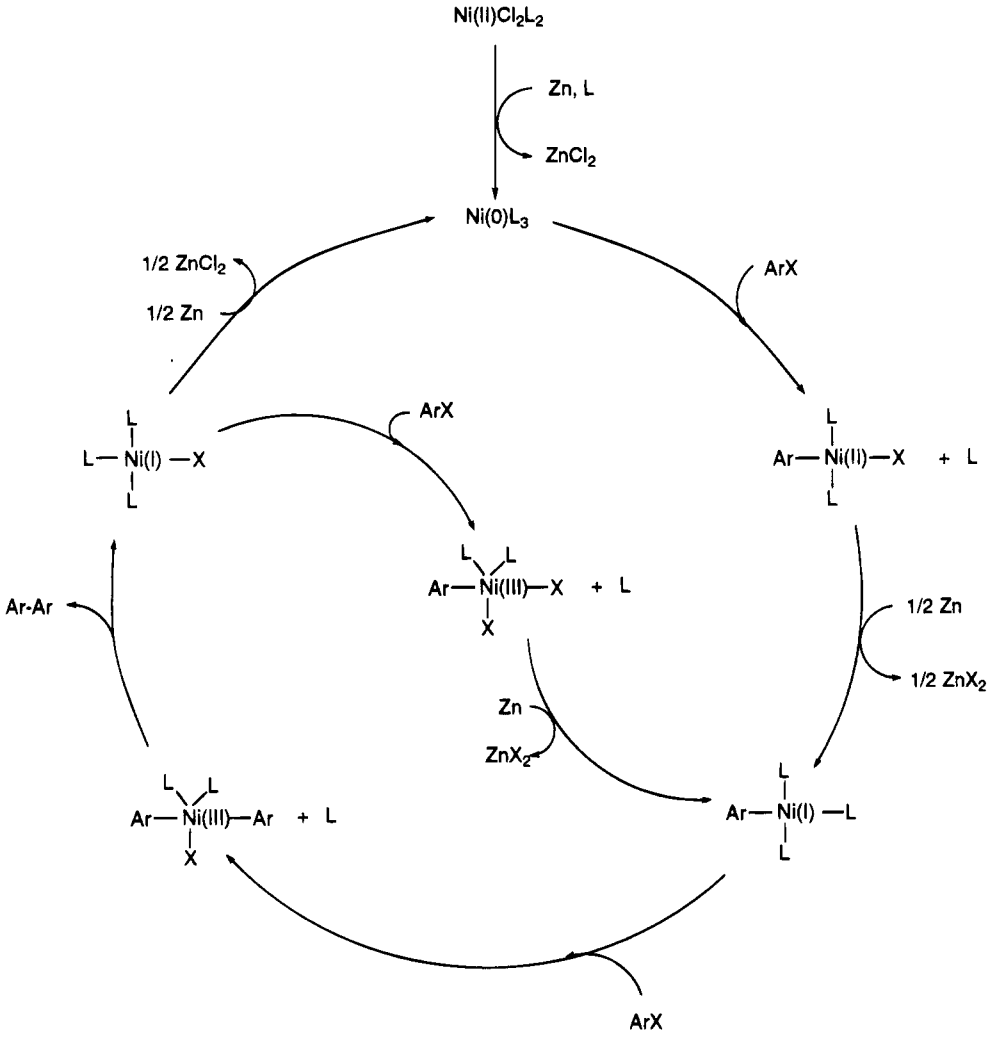
[a] Reaction conditions: 1.0 equiv of Zn, 100 °C, 3 h. [b] Wet DMAc. [c] 1.7 equiv of Zn, 67 °C, 10 h.

this reason, reduced amounts of PPh_3 can be used. Since excess PPh_3 can retard the transition metal-catalyzed coupling reaction and the difficulty of separating excess PPh_3 from the reaction can give lower isolated yield than the actual one, we employed THF as solvent for most studies in order to reduce the amount of excess PPh_3. However, using the coordinatively unsaturated Ni(0) catalyst generated from $NiCl_2(PPh_3)_2$, with no additional PPh_3, required the addition of a halide such as Et_4NI to obtain high yields. Et_4NI can function as a donor ligand stabilizing the Ni(0) catalyst and/or arylnickel species, as well as facilitate the electron transfer process (*vide supra*). However, for successful coupling, severe anhydrous reaction conditions were essential with this system (entry 1 vs 22). We also demonstrated that iodide can be replaced by additional PPh_3, which might mean that the major role of iodide is stabilizing the Ni(0) catalyst and/or aryl nickel species (entry 1 vs 17), *vide supra*. The advantage of additional PPh_3 over iodide was that small amounts of water were tolerable in the coupling reaction (entry 17 vs 18). It is likely that in less polar solvents such as THF, small amounts of water do not impede the coupling reaction greatly. Further studies using wet THF as solvent in combination with other nucleophilic solvents such as pyridine and tetrahydrothiophene as ligand were performed. In the absence of additional PPh_3 or iodide, the coupling reaction did not proceed with wet THF (0% yield, entry 21) due to the immediate deactivation of the catalyst. However, addition of 20 mol % of pyridine or tetrahydrothiophene (based on substrate) to the reaction substantially enhanced the stability of the catalyst resulting in high yield (83% and 53%, respectively, entries 25 and 26). The use of pyridine as both solvent and ligand instead of THF gave moderate yield (55% yield, entry 27). On the other hand, straight tetrahydrothiophene did not give any homocoupled product, probably due to the poor solubility of nickel catalyst and Zn (entry 28). The use of $NiCl_2$ together with other ligands such as pyridine, tetrahydrothiophene and 2,2′-dipyridyl except PPh_3 failed to give homocoupled product (entries 29–31).

Comparison of the THF Method with Dipolar Aprotic Solvent Method. In summary, the most efficient Ni(0) catalyst used was generated from $NiCl_2(PPh_3)_2$ (10 mol %), Et_4NI (1.5 equiv), and Zn (1.7 equiv) in THF at 67 °C. These results need to be compared with those obtained using the system which was used in the reported Ni(0)-catalyzed coupling of 4-acetylphenyl methanesulfonate.[18h] This system typically involved the generation of a Ni(0) catalyst from $NiCl_2(PPh_3)_2$ (5.3%), PPh_3 (20%), an alkaline metal halide salt (1.0 equiv), and Zn (1.0 equiv) in DMAc (or another dipolar aprotic solvent) at 100 °C.[18h] The effect of various reaction conditions is summarized in Table 5. The reaction time is much shorter in the DMAc system (3 h vs 10 h in THF). The reaction yields in DMAc were virtually unchanged at 80 °C (96% vs 95%, entries 1 and 2). Conversely, an increase in temperature to 120 °C resulted in a significant decrease in yield (65% yield, entry 3). The best results were obtained using NaBr as the halide source (96% yield, entry 1). Lower yields were obtained with iodide ions. NaI and KI were much more effective iodide sources than Et_4NI (91%, 93%, and 85% yields, respectively, entries 4, 5, and 6). DMAc was a more effective solvent than DMF (69% yield, entry 7). No coupled product was obtained in NMP (entry 8). When the reaction was performed in the absence of a halide source a low yield of coupled product (16%, entry 9) was obtained. This yield was increased when the amount of PPh_3 was doubled (55% yield, entry 10). The coupling reaction in DMAc was very sensitive to the dryness of the solvent, as yields were dramatically reduced when wet (i.e., not dried over CaH_2) DMAc was used (40% yield with NaBr, 17% yield with KI, entries 11 and 12, respectively).

The selection of a general method (THF or DMAc methods) depends on the exact substrate undergoing the coupling reaction. For example, in the case of 4-acetylphenyl mesylate, the best results were obtained using the reaction conditions typically used with DMAc. The yield of coupled product was 96% in DMAc (entry 1) versus 73% in THF (entry 13). The DMAc system also has the advantage of a shorter reaction time and the use of a more readily available halide source. Alternatively, in the coupling reaction of methyl 4-[(methylsulfonyl)-oxy]benzoate the typical THF reaction conditions gave the best results. The yield of coupled product in this case was >99% (Table 4, entry 1) compared to yields of 78% and 79% obtained in DMAc (Table 4, entries 32 and 33). In this case, the THF system has the further advantage

Scheme 1

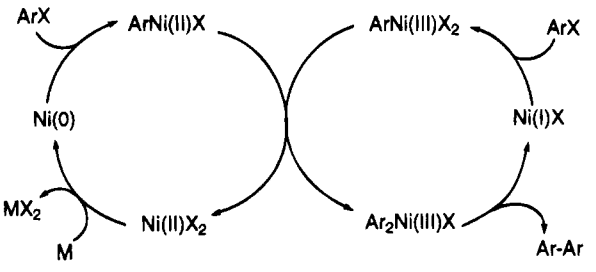


that no extra PPh_3 is necessary under anhydrous conditions and that the reaction can be performed in wet THF when PPh_3 is added (90% yield, Table 4, entry 24).

Reaction Mechanism. Several different reaction mechanisms have been suggested for Ni(0)-catalyzed homocoupling reactions of aryl halides.[2f,28,29] The mechanism outlined in Scheme 1 has been proposed for the Ni(0)-mediated coupling reaction of aryl chlorides in polar aprotic solvents in the presence of excess Zn.[2f] The mechanistic details have been supported by a comprehensive electrochemical study.[29] The mechanism outlined in Scheme 2 has been proposed for the coupling reaction of ArX (X = halide) in nonpolar solvents in the absence of excess reducing metal.[28] The primary mechanistic pathway followed is highly dependent on the reaction conditions.[2c] Under the conditions utilized for the coupling of aryl mesylates, the most plausible mechanism is shown in Scheme 1.[2f,29]

The catalytic cycle shown in Scheme 1 can serve as a working model for a mechanistic discussion of the coupling reaction. The first step of the mechanism involves the reduction of Ni(II) to Ni(0) by Zn. This is followed by the oxidative addition of ArX (X = mesylate or other

Scheme 2



sulfonate leaving group) to the Ni(0) species. This Ni(II) species may have an ionic structure, i.e., $[ArNi(PPh_3)_2]^+[OMs]^-$. The oxidative addition of vinyl triflates to $Pt(PPh_3)_4$ results in the formation of the ionic Pt(II) complexes containing a σ-vinyl ligand, three phosphine ligands, and a noncoordinating triflate anion.[30] A similar Pd(II) complex $[ArPdL_n]^+[OTf]^-$ has been proposed to result from the oxidative addition of ArOTf to Pd(0) in the presence of PPh_3.[31] In a reaction analogous to the reaction of $[RPtL_3]^+[OTf]^-$ with R_4NX,[30] the ArNi(II)OMs

(29) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203.

(30) Kowalski, M. H.; Stang, P. J. *Organometallics* **1986**, *5*, 2392.

(31) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296.

complex may react quickly with Et_4NI to form $ArNi(II)(I)(PPh_3)_2$. The Ni(II) species then undergoes a one-electron reduction to $ArNi(I)L_3$ (L = PPh_3 or THF). ArX oxidatively adds to this species to give a diarylNi(III) complex which undergoes rapid reductive elimination, resulting in the formation of the biaryl product and the generation of $Ni(I)XL_3$. There are two productive reaction pathways available to this Ni species. $Ni(I)XL_3$ can be reduced by Zn to regenerate $Ni(0)L_3$, which can then repeat the catalytic cycle. Alternatively, ArX can undergo direct oxidative addition to $Ni(I)XL_3$ followed by reduction by Zn to form the $ArNi(I)L_3$ species once again.

Although Scheme 1 shows the most probable sequence of steps, the rate-determining step is ambiguous. The rate of oxidative addition of aryl halides to Ni(0) species is considered to be a fast reaction in other coupling reactions.[2f] The rate-determining step in the homocoupling reaction of aryl chlorides under similar reaction conditions in the presence of excess Zn is the reduction of the arylnickel(II) species to the arylnickel(I) species.[2f] However, at high conversions of ArX, the rate-determining step becomes oxidative addition of ArX to the Ni(I) species.[2f] Thus, the rate constants for these reactions are within 1 order of magnitude of each other. When the reduction occurs by electrochemical means, rather than via Zn, the rate-determining step at low concentrations of ArBr is oxidative addition of ArBr to the ArNi(I) species and at higher concentrations of ArBr is the reductive elimination of biaryl from the Ni species.[29]

The highest yields in the coupling reaction of aryl mesylates were obtained with electron-withdrawing groups in the para position. The reaction was inhibited by electron-donating groups as well as by sterically hindering ortho groups. However, these effects alone cannot be used to determine the rate-determining step. Electron-withdrawing groups can increase the rate of oxidative addition of aryl halides to Ni(0).[25] The rate of oxidative addition is also influenced by the nature of the leaving group.[25] The electronic properties of the aryl group have also been shown to influence the reactivity of $[ArPdL_n]^+[OTf]^-$.[31] Thus, it is possible that the electronic properties of the aryl group could affect the rate of electron transfer in the reduction of the arylnickel(II) species to an arylnickel(I) species. Furthermore, the rate of reductive elimination is increased by positive charge.[1e] Thus, the electron-donating groups could slow the reductive elimination step.

The presence of sterically hindering ortho groups can also influence the rate of several steps. For example, the oxidative addition of ArX to ArNi(I) would be expected to proceed more slowly with ortho substituents on the aryl groups. In addition, the rate of electron transfer to ArNi(II) could also be affected by an ortho substituent, especially if a bridging I^- ion is involved.

Another possibility is that the mechanism is similar to the one proposed by Tsou and Kochi, a double-chain mechanism involving the reaction of $ArNi^{III}X_2$ and $ArNi^{II}X$ to form $Ar_2Ni^{III}X$ in the key step (Scheme 2).[28] Evidence for this mechanism was obtained using nonpolar solvents such as benzene, toluene, and hexane. The bimolecular step involves Ni species expected to be present in trace quantities when excess Zn is present. Thus, this mechanism is expected to be favored when large amounts of Ni catalyst and small amounts of Zn are present. This mechanism may have some contribution at high conversions when all aryl sulfonate has been consumed but before all of the arylnickel species have reacted to give the coupled product.

Conclusions

The experiments reported here demonstrate that most aryl sulfonates including aryl mesylate undergo Ni(0)-catalyzed homocoupling reactions in THF, dioxane, and DMAc, generating functional symmetrical biaryls in high yields. The application of this very convenient synthetic method to the preparation of well known 2,2′-, 3,3′-, and 4,4′-biphenyls and -biaryls from readily available phenols and of novel biaryls has been demonstrated. The most reactive leaving group, which is comparable in reactivity with triflate, is the *p*-fluorobenzenesulfonate group. However, excellent to good yields were obtained with the inexpensive mesylate group. The highest yields were obtained when the aryl group had electron-withdrawing substituents in para position. Yields were reduced slightly when an *o*-substituent was present and the extent of side reactions increased in this case. The identified side reactions were reduction and transarylation of the aryl mesylate. When the *o*-substituent contains an ester or carbonyl group attached to the aryl mesylate the steric effect is partially released. Because substituted phenols, hydroquinones, and bisphenols are readily accessible, the mesylate leaving group provides an extremely convenient access to already known and to new functionalized symmetrical biaryls.

Experimental Section

General Methods. Melting points are uncorrected and were determined with a capillary melting point apparatus or a Perkin-Elmer DSC-7 equipped with a TAC 7/DX thermal analysis controller at 20 °C/min. ^{1}H-NMR (200-MHz) and ^{13}C-{^{1}H} (50-MHz) spectra were recorded on a Varian XL-200 spectrometer. EIMS were recorded at 20–50 eV ionizing energy. HRMS were obtained with a Kratos MS25RFA instrument. GC analyses were performed on a HP 5890 gas chromatograph using a flame ionization detector and a 3% SP-2250 column. Yields were determined by GC (diphenyl ether as an internal standard) and in some cases by ^{1}H-NMR spectroscopy. HPLC measurements were performed on a Perkin-Elmer Series 10 LC instrument equipped with an LC-100 oven and a Nelson Analytical 900 Series data station. The measurements were made using a UV detector set at 254 nm with THF as solvent (1 mL/min, 40 °C) using a 100-Å PL gel column. TLC analyses were performed on polyester sheets precoated with 0.25 mm thick silica gel containing a 254-nm indicator (Kodak 13181). Column chromatographic purifications were performed with 32–63 mesh ICN silica gel or activated basic Brockmann I 150 mesh aluminum oxide.

All reagents, including phenols and hydroquinones, were purchased from commercial sources (Aldrich or Lancaster) and used without further purification except when reported. Pyridine was dried over CaH_2 and distilled. THF and dioxane were distilled from sodium benzophenone ketyl. Zinc dust was stirred in acetic acid, washed with water, and dried in vacuo at 120 °C. $NiCl_2(PPh_3)_2$ was prepared according to a literature procedure.[32]

Purities. Unless otherwise noted, all compounds synthesized in the present paper were purified until their 200 MHz ^{1}H-NMR spectra corresponded to the expected structure and the purity was established by comparison with published mp or found to be higher than 99.5% by GC or HPLC.

Aryl Triflates and Aryl Arenesulfonates. Aryl triflates[10a] were synthesized by the reaction of triflic anhydride with the corresponding phenol in pyridine, and aryl arenesulfonates

(32) (a) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719. (b) Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L. *J. Am. Chem. Soc.* **1961**, *83*, 344.

were synthesized by the reaction of the arenesulfonyl chloride with the corresponding phenol in pyridine, unless otherwise noted.

Methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (85%): purified by column chromatogaphy, (SiO_2, Hexanes/Et_2O 1:1), and vacuum distilled; colorless oil; bp 71–73 °C/0.3 mmHg (lit.[33] bp 93–95 °C/1.4 mmHg); ^1H NMR δ 8.14 (d, J = 7.4 Hz, 2H), 7.39 (d, J = 7.4 Hz, 2H), 3.95 (s, 3H).

Methyl 4-(((4-fluorophenyl)sulfonyl)oxy)benzoate (90%): white crystals; mp 80–82 °C (hexanes); ^1H NMR δ 7.99 (d, J = 8.5 Hz, 2H), 7.87 (dd, J = 9.0, 5.0 Hz, 2H), 7.22 (dd, J = 8.5, 8.3 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 3.91 (s, 3H); $^{13}C\{^1H\}$ NMR δ 166.00 (d, $^1J_{CF}$ = 258 Hz), 165.66, 152.56, 131.28, 131.27 (d, $^3J_{CF}$ = 9.6 Hz), 130.89 (d, $^4J_{CF}$ = 3Hz), 129.04, 122.12, 116.61 (d, $^2J_{CF}$ = 23 Hz), 52.22; EIMS m/e 310 (M^+, 32), 279 (6), 175 (6), 159 (100), 123 (15), 95 (89); HRMS calcd for $C_{14}H_{11}FO_5S$ 310.0311, found 310.0323.

Methyl 4-(((4-chlorophenyl)sulfonyl)oxy)benzoate (83%): white crystals; mp 95–96 °C (hexanes); ^1H NMR δ 7.99 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.67, 152.54, 141.22, 133.38, 131.33, 129.76, 129.57, 129.11, 122.12, 52.26; EIMS m/e 326 (M^+, 37), 295 (6), 175 (100), 123 (13), 111 (79); HRMS calcd for $C_{14}H_{11}ClO_5S$ 326.0016, found 326.0017.

Methyl 4-((phenylsulfonyl)oxy)benzoate (79%): white crystals; mp 63–64 °C (hexanes); ^1H NMR δ 7.96 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 7.73–7.66 (m,1H), 7.58–7.50 (m, 2H), 7.09 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.69, 152.65, 134.82, 134.40, 131.16, 129.16, 128.86, 128.26, 122.14, 52.18; EIMS m/e 292 (M^+, 28), 141 (72), 123 (9), 77 (100); HRMS calcd for $C_{14}H_{12}O_5S$ 292.0405, found 292.0259.

Methyl 4-(((4-methylphenyl)sulfonyl)oxy)benzoate (75%): white crystals; mp 85–86 °C (hexanes) (lit.[34] mp 84–85 °C); ^1H NMR δ 7.96 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H), 2.45 (s, 3H).

4-Acetylphenyl *p*-fluorobenzenesulfonate (85%): white crystals; mp 77–79 °C (hexanes) (lit.[20] mp 75–77 °C); ^1H NMR δ 7.95–7.84 (m, 4H), 7.28 –7.20 (m, 2H), 7.13 (d, J = 8.7 Hz, 2H), 2.59 (s, 3H).

Methyl 2-(((4-fluorophenyl)sulfonyl)oxy)benzoate (85%): white crystals; mp 87–88 °C (hexanes); ^1H NMR δ 7.93–7.86 (m, 3H), 7.54–7.12 (m, 5H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.86 (d, $^1J_{CF}$ = 258 Hz), 164.59, 147.44, 133.29, 131.84, 131.39, 131.21, 127.12, 125.10, 123.62, 116.32 (d, $^2J_{CF}$ = 23 Hz), 52.15; EIMS m/e (%) 310 (M^+, 57), 279 (19), 205 (14), 159 (80), 120 (100), 95 (91); HRMS calcd for $C_{14}H_{11}FO_5S$ 310.0311, found 310.0311.

4-Biphenylyl *p*-fluorobenzenesulfonate (64%): white crystals; mp 117–118 °C (hexanes); ^1H NMR δ 7.89 (dd, J = 7.4, 5.1 Hz, 2H), 7.54–7.36 (m, 7H), 7.22 (dd, J = 7.4, 7.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR δ 165.96 (d, $^1J_{CF}$ = 257 Hz), 148.71, 140.35, 139.52, 131.45, 131.26, 128.83, 128.27, 127.69, 126.98, 122.51, 116.53 (d, $^2J_{CF}$ = 23 Hz); EIMS m/e 328 (M^+, 32), 170 (16), 141 (25), 120 (7), 95 (8); HRMS calcd for $C_{18}H_{13}FO_3S$ 328.0569, found 328.0559.

Phenyl *p*-fluorobenzenesulfonate (71%): colorless oil, purified by column chromatography (SiO_2, hexanes/ether 1:1) and vacuum distilled; bp 123–125 °C/0.36 mmHg (lit.[35] bp 95–96 °C/0.08 mmHg); ^1H NMR δ 7.85 (dd, J = 7.1, 5.0 Hz, 2H), 7.31–7.16 (m, 5H), 7.00 (d, J = 7.8 Hz, 2H).

4-Tolyl *p*-fluorobenzenesulfonate (88%): white crystals; mp 83–84 °C (hexanes) (lit.[36] mp 85–86 °C); ^1H NMR δ 7.86 (dd, J = 8.9, 5.0 Hz, 2H), 7.20 (dd, J = 8.9, 8.6 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 2.31 (s, 3H).

2-Tolyl *p*-fluorobenzenesulfonate (80%): white crystals; mp 64–65 °C (hexanes); ^1H NMR δ 7.88 (dd, J = 7.1, 5.1 Hz, 2H), 7.26–7.01 (m, 6H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.90 (d, $^1J_{CF}$ = 257 Hz), 148.06, 132.02 (d, $^4J_{CF}$ = 2.7 Hz), 131.60, 131.35, 131.13 (d, $^3J_{CF}$ = 9.8 Hz), 127.09, 126.91, 122.07, 116.47 (d, $^2J_{CF}$ = 23 Hz), 16.12; EIMS m/e 266 (M^+, 62), 159 (97), 107 (100), 95 (67), 77 (39); HRMS calcd for $C_{13}H_{11}FO_3S$ 266.0413, found 266.0410.

4-Methoxyphenyl *p*-fluorobenzenesulfonate (94%): white crystals; mp 66–67 °C (hexanes); ^1H NMR δ 7.84 (dd, J = 8.9, 5.0 Hz, 2H), 7.20 (dd, J = 8.9, 8.5 Hz, 2H), 6.87 (d, J = 9.3 Hz, 2H), 6.81 (d, J = 9.3 Hz, 2H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.82 (d, $^1J_{CF}$ = 257 Hz), 158.20, 142.67, 131.28 (d, $^3J_{CF}$ = 9.7 Hz), 131.03 (d, $^4J_{CF}$ = 3.0 Hz), 123.12, 116.39 (d, $^2J_{CF}$ = 23 Hz), 114.43, 55.39; EIMS m/e 282 (M^+, 18), 123 (100), 95 (14); HRMS calcd for $C_{13}H_{11}FO_4S$ 282.0362, found 282.0361.

4-Tolyl benzenesulfonate (90%): white crystals; mp 50–51°C (hexanes) (lit.[37] mp 48–49 °C); ^1H NMR δ 7.82 (d, J = 7.5 Hz, 2H), 7.71–7.63 (m, 1H), 7.56–7.48 (m, 2H) 7.05 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 2.30 (s, 3H).

4-Methoxyphenyl benzenesulfonate (73%): colorless oil, purified by column chromatography (SiO_2, hexanes/Et_2O 1:1) and vacuum distilled; bp 152–154 °C/0.03 mmHg; ^1H NMR δ 7.80 (d, J = 7.7 Hz, 2H), 7.70–7.63 (m, 1H), 7.55–7.48 (m, 2H), 6.85 (d, J = 9.2 Hz, 2H), 6.78 (d, J = 9.2 Hz, 2H), 3.74 (s, 3H); $^{13}C\{^1H\}$ NMR δ 158.01, 142.65, 134.89, 134.04, 128.92, 128.19, 123.01, 114.25, 55.23; EIMS m/e 264 (M^+, 72), 123 (100), 95 (35), 77 (22); HRMS calcd for $C_{13}H_{12}O_4S$ 264.0456, found 264.0450.

Aryl mesylates were prepared by the reaction of methanesulfonyl chloride with the corresponding phenols in pyridine.[38]

Methyl 4-((methylsulfonyl)oxy)benzoate (92%): white crystals; mp 89–90 °C (hexanes); ^1H NMR δ 8.10 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 3.94 (s, 3H), 3.19 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.67, 152.32, 131.51, 129.04, 121.76, 52.23, 37.64; EIMS m/e 230 (M^+, 65), 199 (40), 152 (89), 121 (100), 92 (20), 63 (19); HRMS calcd for $C_9H_{10}O_5S$ 230.0249, found 230.0255.

Methyl 3-((methylsulfonyl)oxy)benzoate (81%): white crystals; mp 70–72 °C (hexanes); ^1H NMR δ 8.04–7.94 (m, 2H), δ 7.54–7.51 (m, 2H), 3.94 (s, 3H), 3.20 (s, 3H); $^{13}C\{^1H\}$ NMR δ 165.37, 148.88, 132.06, 129.95, 128.25, 126.51, 122.83, 52.29, 37.38; EIMS m/e 230 (M^+, 53), 152 (100), 121 (64), 92 (24); HRMS calcd for $C_9H_{10}O_5S$ 230.0249, found 230.0249.

Methyl 2-((methylsulfonyl)oxy)benzoate (81%): colorless oil, purified by column chromatography (SiO_2, hexanes/Et_2O 1:1) and vacuum distilled; bp 120–123 °C/0.004 mmHg; ^1H NMR δ 7.97 (d, J = 7.6 Hz, 1H), 7.63–7.56 (m, 1H), 7.47–7.36 (m, 2H), 3.93 (s, 3H), 3.28 (s, 3H); $^{13}C\{^1H\}$ NMR δ 164.51, 147.53, 133.61, 131.84, 126.99, 124.24, 123.83, 52.23, 38.11; EIMS m/e 230 (M^+, 26), 199 (14), 152 (54), 120 (100), 92 (31), 64 (16); HRMS calcd for $C_9H_{10}O_5S$ 230.0249, Found 230.0014.

4-Acetylphenyl methanesulfonate (83%): yellow crystals; mp 71–72 °C (hexanes) (lit.[39] mp 70–71 °C); ^1H NMR δ 8.02 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 3.20 (s, 3H), 2.62 (s, 3H).

4-Cyanophenyl methanesulfonate (82%): white crystals; mp 89–90 °C (hexanes); ^1H NMR δ 7.73 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 3.24 (s, 3H); $^{13}C\{^1H\}$ NMR δ 151.77, 134.10, 122.90, 117.54, 111.19, 37.97; EIMS m/e 197 (M^+, 56), 133 (9), 120 (16), 90 (46), 79 (100), 64 (22); HRMS calcd for $C_8H_7NO_3S$ 197.0147, found 197.0145.

4-Fluorophenyl methanesulfonate (58%): colorless oil, purified by column chromatography (SiO_2, hexanes/Et_2O 1:1) and vacuum distilled; ^1H NMR δ 7.28 (dd, J =9.3, 3.9 Hz, 2H), 7.12 (dd, J = 9.3, 8.6 Hz, 2H), 3.16 (s, 3H); $^{13}C\{^1H\}$ NMR δ 160.97 (d, $^1J_{CF}$ = 247 Hz), 144.80, 123.61 (d, $^3J_{CF}$ = 8 Hz), 116.55 (d, $^2J_{CF}$ = 24 Hz), 37.00; EIMS m/e 190 (M^+, 47), 119

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(21), 112 (100), 83 (71), 57 (25); HRMS calcd for $C_7H_7FO_3S$ 190.0100, found 190.0171.

4-Nitrophenyl methanesulfonate (91%): pale brown needles; mp 93–94 °C (lit.[40] mp 93–93.5 °C); ^1H NMR δ 8.33 (d, J = 9.1 Hz, 2H), 7.48 (d, J = 9.1 Hz, 2H), 3.26 (s, 3H).

Phenyl methanesulfonate (91%): white crystals; mp 62–63 °C (hexanes) (lit.[41] mp 61.5 °C); ^1H NMR δ 7.44–7.28 (m, 5H), 3.14 (s, 3H).

4-Biphenylyl methanesulfonate (92%): white crystals; mp 146–148 °C (Et_2O); ^1H NMR δ 7.64–7.41 (m, 7H), 7.38 (d, J = 8.0 Hz, 2H), 3.18 (s, 3H); $^{13}C\{^1H\}$ NMR δ 148.51, 140.57, 139.66, 128.86, 128.63, 127.71, 127.07, 122.24, 37.32; EIMS m/e 248 (M^+, 80), 170 (55), 141 (100), 115 (28); HRMS calcd for $C_{13}H_{12}O_3S$ 248.0507, found 248.0508.

4-Tolyl methanesulfonate (75%): white crystals; mp 46–48 °C (hexanes) (lit.[42] mp 44.5–46 °C); ^1H NMR δ 7.20 (d, J = 9.2 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 3.12 (s, 3H), 2.36 (s, 3H).

4-Methoxyphenyl methanesulfonate (77%): white crystals; mp 78–80 °C (hexanes) (lit.[41] mp 77–79 °C); ^1H NMR δ 7.19 (d, J = 7.1 Hz, 2H), 6.93 (d, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.11 (s, 3H).

Pentafluorophenyl methanesulfonate (96%): colorless oil; ^1H NMR δ 3.10 (s, 3H); $^{13}C\{^1H\}$ NMR δ 142.18 (d, $^1J_{CF}$ = 254 Hz), 140.36 (d, $^1J_{CF}$ = 257 Hz), 137.93 (d, $^1J_{CF}$ = 257 Hz), 123.94, 39.18; EIMS m/e 262 (M^+, 74), 198 (27), 184 (82), 155 (53), 79 (100); HRMS calcd for $C_7H_3F_5O_3S$ 261.9723, found 261.9632.

6-Carbomethoxy-2-naphthyl methanesulfonate (84%): white crystals (benzene); mp 114 °C (hexanes); ^1H NMR δ 8.58 (s, 1H), 8.06 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 10 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.76 (s, 1H), 7.46 (d, J = 10 Hz, 1H), 3.98 (s, 3H), 3.22 (s, 3H); $^{13}C\{^1H\}$ NMR δ 166.73, 148.34, 135.76, 131.71, 131.02, 130.73, 128.10, 126.46, 121.64, 119.29, 52.34, 37.65; EIMS m/e 280 (M^+, 70), 201 (74), 173 (100), 142 (49), 114 (72); HRMS calcd for $C_{13}H_{12}O_5S$ 280.0405, found 280.0416.

General Procedure for Homocoupling Reaction of Aryl Sulfonates. All reactions were carried out under nitrogen using oven-dried (110 °C) glassware. In a typical reaction a 125 mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (0.10 mmol), Zn powder (1.7 mmol), Et_4NI (1.5 mmol), and a magnetic stirring bar. After the tube was sealed with a rubber septum, the contents were dried at 22 °C under reduced pressure (1×10^{-3} mmHg) for 10 h. The contents of the tube were then placed under an Ar atmosphere by filling with Ar followed by three evacuation–filling cycles. Freshly distilled THF (0.50 mL) was added via a syringe through the rubber septum. The mixture was stirred at room temperature for 5 min, and during this time the color of the mixture gradually became deep red-brown. Aryl sulfonate (1.0 mmol) was dissolved in freshly distilled THF (0.50 mL) and added to the catalyst mixture via a syringe through the rubber septum. The reaction mixture was heated to the reflux temperature and stirred at this temperature for 5–10 h. The reaction mixture was then cooled, filtered, diluted with water, extracted with $CHCl_3$, dried ($MgSO_4$) and the solvent evaporated *in vacuo*. The corresponding biaryl was obtained after column chromatography (silica gel, *n*-hexane/ethyl acetate) and recrystallization from $CHCl_3$/hexanes.

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Biaryls. 4,4′-Dicarbomethoxybiphenyl: white crystals; mp 214–216 °C (benzene) (lit.[43] mp 215–217 °C); ^1H NMR δ 8.12 (d, J = 8.4 Hz, 4H), 7.72 (d, J = 8.4 Hz, 4H), 3.96 (s, 6H).

4,4′-Diacetylbiphenyl: pale yellow crystals; mp 190–193 °C (benzene) (lit.[44] mp 191 °C); ^1H NMR δ 8.06 (d, J = 8.3 Hz, 4H), 7.76 (d, J = 8.3 Hz, 4H), 2.66 (s, 6H).

2,2′-Dicarbomethoxybiphenyl: white crystals; mp 69–71 °C (hexanes) (lit.[45] mp 73–74 °C); ^1H NMR δ 8.00 (d, J = 6.7 Hz, 2H), 7.55 (dd, J = 7.5, 5.9 Hz, 2H), 7.43 (dd, J = 7.5, 7.4 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 3.62 (s, 6H).

***p*-Quaterphenyl**: white crystals; mp 319 °C ($CHCl_3$) (by DSC, lit.[46] mp 320 °C).

Biphenyl: white solid; mp 70–71 °C (hexanes) (lit.[47] mp 71 °C); ^1H NMR δ 7.58 (d, J = 7.0 Hz, 4H), 7.48–7.31 (m, 6H).

4,4′-Dimethylbiphenyl: white crystals; mp 120–122 °C (hexanes) (lit.[48] mp 121 °C); ^1H NMR δ 7.46 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H), 2.39 (s, 6H).

2,2′-Dimethylbiphenyl: colorless oil purified by column chromatography (SiO_2 hexanes) vacuum distilled; bp 80–83 °C/0.8 mmHg (lit.[49] bp 69 °C/0.5 mmHg); ^1H NMR δ 7.38–7.05 (m, 8H), 2.05 (s, 6H).

4,4′-Dimethoxybiphenyl: white crystals; mp 174–176 °C (hexanes) (lit.[50] mp 176.5–177 °C); ^1H NMR δ 7.46 (d, J = 8.8 Hz, 4H), 6.99 (d, J = 8.8 Hz, 4H), 3.85 (s, 6H).

3,3′-Dicarbomethoxybiphenyl: white crystals; mp 100–102 °C (hexanes) (lit.[51] mp 103 °C); ^1H NMR δ 8.32 (s, 2H), 8.04 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.74–7.64 (m, 2H), 3.96 (s, 6H).

4,4′-Dicyanobiphenyl: white crystals; mp 229–230 °C (benzene) (lit.[43] mp 232–234 °C); ^1H NMR δ 7.78 (d, J = 8.6 Hz, 4H), 7.72 (d, J = 8.5 Hz, 4H).

4,4′-Difluorobiphenyl: white crystals; mp 88–89 °C (hexanes) (lit.[52] mp 87–89 °C); ^1H NMR δ 7.49 (dd, J = 8.8, 5.2 Hz, 4H), 7.12 (dd, J = 8.8, 8.7 Hz, 4H).

6,6′-Dicarbomethoxy-2,2′-dinaphthyl: white crystals; mp 275 °C ($CHCl_3$); ^1H NMR δ 8.65 (s, 2H), 8.23 (s, 2H), 8.17–8.09 (m, 4H), 8.02–7.94 (m, 4H), 4.03 (s, 6H). Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.16; H, 4.81.

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Supplementary Material Available: ^1H NMR, $^{13}C\{^1H\}$ NMR, and HRMS spectra of new compounds are listed (48 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 for ordering information.

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