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Nickel- or Cobalt-Catalyzed Cross-Coupling of Arylsulfonic Acid Salts with Grignard Reagents

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Dedicated to Prof. Stephen L. Buchwald on the occasion of his 60th birthday.

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Abstract: The use of arylsulfonic acid salts as electrophiles in a nickel- or cobalt-catalyzed cross-coupling with Grignard reagents is described. Bis(tricyclohexylphosphine)nickel dichloride [$NiCl_2(PCy_3)_2$] was found to be the optimal catalyst, and reactions with this catalyst proceeded in most cases at room temperature. The analogous cobalt catalyst [$CoCl_2(PCy_3)_2$] was also found to promote the cross-coupling reaction at higher temperature (60 °C).

Keywords: cobalt; cross-coupling; Grignard reagents; nickel; sulfonic acids

The electrophiles employed in transition metal-catalyzed cross-coupling reactions have historically been predominantly aryl halides.[1] Alternative, non-halogen electrophiles have been developed, however, and are seeing increased applications in recent years. Phenol-derived electrophiles, including phenolic salts,[2] sulfonates,[3] sulfates,[4] phosphates,[5] ethers,[6] esters,[7] carbamates,[8] carbonates,[8b] and sulfamates[8a–b,9] have been shown to be competent C–O electrophiles in many types of cross-coupling reactions. Arylamine derivatives such as diazonium salts,[10] trimethylammonium salts,[11] triazenes,[12] and even anilines[13] have been developed as C–N based electrophiles. The use of aryl-sulfur derivatives as electrophiles was pioneered by Wenkert and co-workers in 1979, when they extended their work on the Ni-catalyzed coupling of vinyl and aryl ethers with Grignard reagents[6a] to the analogous cross-coupling of vinyl sulfides, aryl thiols, aryl sulfides, aryl sulfoxides, aryl sulfones, and arylsulfinate salts with Grignard reagents.[14] The use of aryl *tert*-butyl sulfones (Julia and co-workers),[15] neopentyl arylsulfonates (Park and co-workers),[16] and *N*,*N*-diethylarylsulfonamides (Snieckus and co-workers)[17] was subsequently reported for Ni-catalyzed cross-coupling with Grignard reagents. Vogel and co-workers have developed several desulfinylative cross-coupling reactions with arylsulfonyl chlorides as the electrophiles.[18] Aryl-sulfur electrophiles have shown compatibility with an array of different transition metal-catalyzed cross-coupling reactions.[19]

Aromatic sulfonylation is one of the fundamental aromatic heterofunctionalization reactions along with halogenation, oxidation and nitration (Figure 1).[20] This reaction was first demonstrated in 1825 when Faraday reported that the treatment of naphthalene with sulfuric acid gave 1- and 2-naphthalenesulfonic acids, which he converted to several different alkali salts.[21] While aryl halides, phenol derivatives and aniline derivatives have been examined as electrophiles in cross-coupling reactions, nitroarenes and arylsulfonic acids, products of two of the fundamental aromatic heterofunctionalization reactions, remain essentially unexplored.[22] Herein we report the cross-coupling of arylsulfonic acid salts with Grignard reagents under mild conditions using $NiCl_2(PCy_3)_2$ or $CoCl_2(PCy_3)_2$ as catalyst.

To screen the feasibility of the reaction with various catalysts, the reaction of sodium benzenesulfonate **1** with 4-methoxyphenylmagnesium bromide (3 equiv)[23] in THF at ambient temperature was employed (Table 1). In the absence of catalyst, no reaction took place (entry 1). Using non-ligated $NiCl_2$

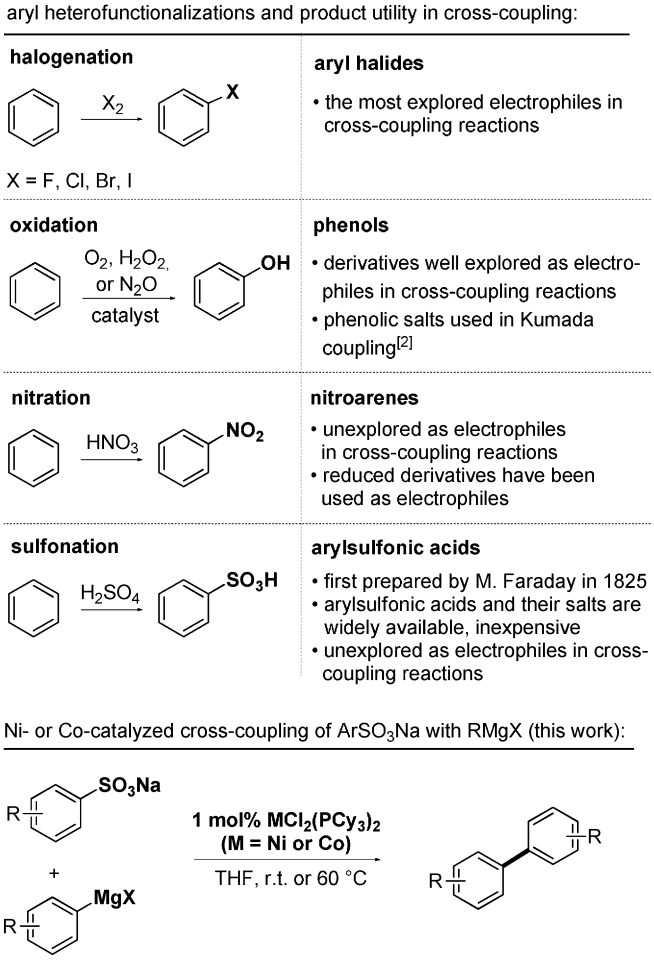


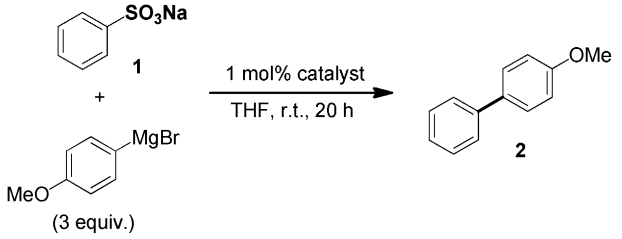
Figure 1. Fundamental methods of aromatic heterofunctionalization and utility of products as electrophiles in cross-coupling reactions.

gave biaryl **2** in 53% yield. The use of $NiCl_2(PPh_3)_2$ as catalyst gave no increase in yield (entry 3). Employing the more electron-rich complex $NiCl_2(PCy_3)_2$ provided a dramatic improvement, furnishing **2** in 98% yield (entry 4). The power of $NiCl_2(PCy_3)_2$ in cross-coupling reactions which necessitate challenging oxidative additions has been well documented.[4,6b,c,7,8,24] Nickel complexes with bidentate ligands (entries 5 and 6) gave **2** in low yields. The use of a palladium complex (entry 7) gave no product. Cobalt catalysis was also investigated. Non-ligated $CoCl_2$ gave a 63% yield of **2** (entry 8), while $CoCl_2(PPh_3)_2$ gave a reduced yield of 38% (entry 9). Interestingly, employing the cobalt complex $[CoCl_2(PCy_3)_2]$ structurally analogous to the most effective nickel catalyst gave a 93% yield when the reaction temperature was raised to 60 °C (entry 10).

The scope of the nickel-catalyzed cross-coupling reaction of sodium benzenesulfonate **1** was explored with respect to variation of the Grignard reagent (Scheme 1). When electron-rich aryl Grignard reagents were employed (products **2**–**4**, **8**, **9**), the reactions proceeded to completion at room temperature within 20 h and provided good yields of biaryl products. Notably, the reaction was also effective when the free sulfonic acid $PhSO_3H$ was used. An additional equivalent of Grignard reagent was employed to deprotonate the sulfonic acid. In the case of the coupling with sterically demanding 2-mesitylmagnesium bromide (product **5**), the reaction required heating to 60 °C to complete within 20 h. Nonetheless, biaryl **5** was obtained in excellent yield (83%). The use of electron-poor aryl Grignard reagents also required raising the reaction temperature to 60 °C to achieve a reasonable reaction rate (products **6** and **7**). The use of aryl Grignard reagents generated from aryl bromides and Mg/LiCl according to Knochel's procedure was also effective (products **8** and **9**).[25]

We next explored the reaction scope with various arylsulfonic acid salts (Scheme 2). The coupling of sodium *p*-toluenesulfonate with PhMgBr required 48 h to reach completion at room temperature, giving **4** in 55% yield. Reaction of the more electron-rich 4-methoxyphenylmagnesium bromide with *p*-TsONa proceeded to completion within 20 h at room temperature to furnish **10** in 72% yield. The coupling of bulky 2-mesitylmagnesium bromide with *p*-TsONa required heating at 60 °C, and gave biaryl **11** in 67% yield. The reaction of more sterically hindered arylsulfonic acid salts, such as sodium 2,4-dimethylben-

Table 1. Catalyst screening results.[a]



Entry	Catalyst	Yield [%][b]
1	none	0
2	$NiCl_2$	53
3	$NiCl_2(PPh_3)_2$	52
4	**$NiCl_2(PCy_3)_2$**	98
5	$NiCl_2$(dppe)[c]	45
6	$NiCl_2$(dppf)[d]	46
7	$PdCl_2(PPh_3)_2$	0
8	$CoCl_2$[e]	63
9	$CoCl_2(PPh_3)_2$[e]	38
10	**$CoCl_2(PCy_3)_2$**[e]	93

[a] *Typical reaction conditions:* 0.5 mmol 1, 1.5 mmol ArMgBr, 1 mol% catalyst, THF, room temperature, 20 h.
[b] HPLC assay yield of **2**.
[c] dppe = 1,2-bis(diphenylphosphino)ethane.
[d] dppf = 1,2-bis(diphenylphosphino)ferrocene.
[e] Reaction performed at 60 °C.

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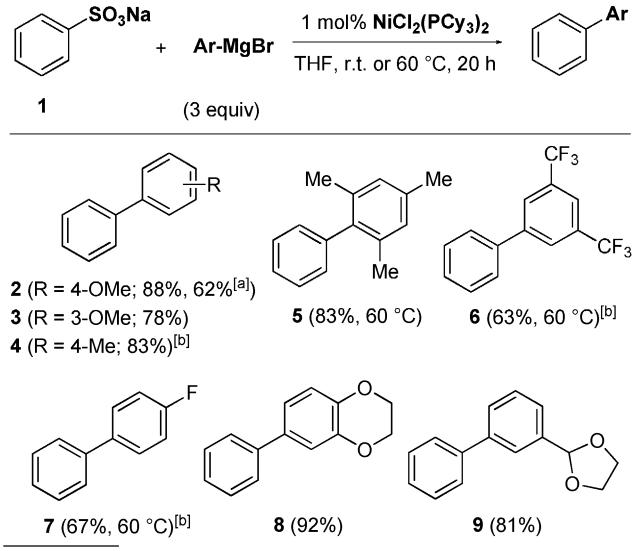
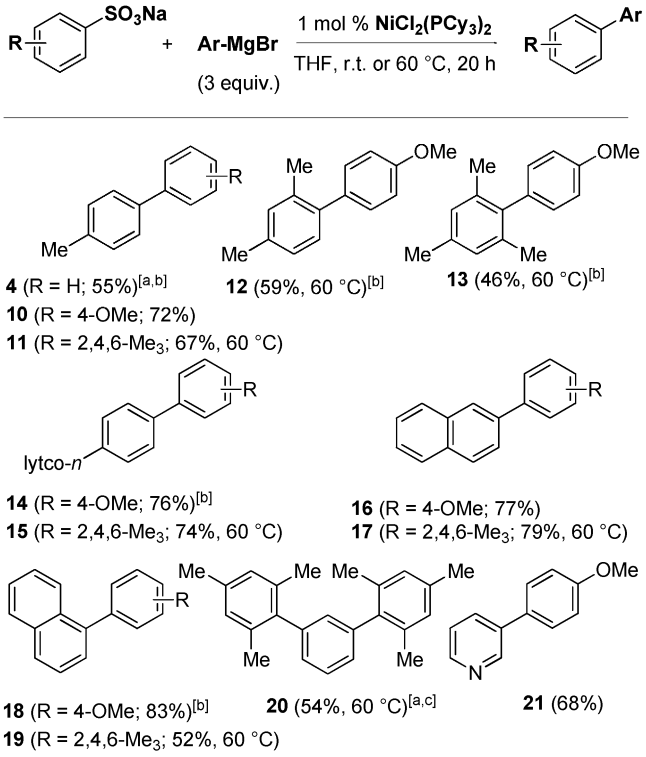


[a] $PhSO_3H$ used instead of $PhSO_3Na$, 8.0 mmol ArMgBr used.
[b] GC assay yield *vs.* dodecane as internal standard.

Scheme 1. Scope of Ni-catalyzed coupling of **1** with different aryl Grignard reagents. *Reaction conditions:* 2.0 mmol **1**, 6.0 mmol ArMgBr, 1 mol% $NiCl_2(PCy_3)_2$, THF, room temperature or 60 °C, 20 h. Isolated yields unless noted otherwise.

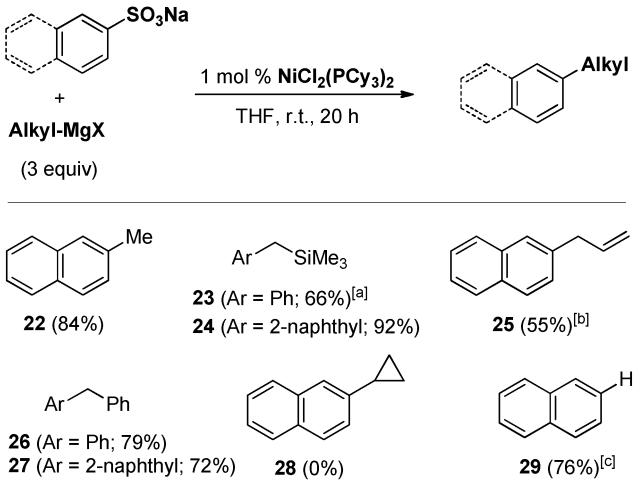
zenesulfonate and sodium 2-mesitylenesulfonate, also required heating at 60 °C to give products **12** and **13** in moderate yields. To the best of our knowledge, the use of either a sterically hindered 2-mesityl Grignard as nucleophile or of a 2-mesityl electrophile is unprecedented with a sulfur-derived electrophile in a Kumada coupling. The highly lipophilic sodium 4-*n*-octylbenzensulfonate coupled well with both 4-methoxyphenyl- and 2-mesitylmagnesium bromide to give **14** and **15** in good yields. Sodium 2-naphthalenesulfonate and sodium 1-naphthalenesulfonate reacted smoothly to yield products **16**–**19** in good yields. Sodium benzene-1,3-disulfonate reacted with 6 equiv. of 2-mesitylmagnesium bromide to give the sterically hindered terphenyl **20** in 54% yield. The cross-coupling also worked with the heterocyclic sodium 3-pyridinesulfonate to yield biaryl **21** in good yield.

The Ni-catalyzed cross-coupling reaction could also be extended to alkyl Grignard reagents (Scheme 3). Sodium 2-naphthalenesulfonate coupled smoothly with MeMgCl, Me_3SiCH_2MgCl, allylMgCl, and BnMgCl at room temperature, providing the corresponding products **22**, **24**, **25** and **27** in good yields. In the case of the allylMgCl coupling, the product **25** was partially isomerized under the reaction conditions to the conjugated isomeric compound (*E*)-2-(prop-1-en-1-yl)naphthalene. $PhSO_3Na$ also coupled with Me_3SiCH_2MgCl and BnMgCl to give products **23** and **26** in good yields. Interestingly, the reaction with cyclopropyl-magnesium bromide failed to give any con-



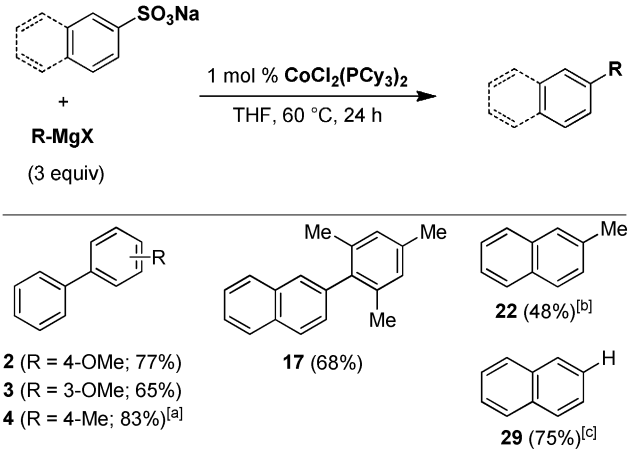
[a] Reaction time of 48 h.
[b] GC assay yield *vs.* dodecane as internal standard.
[c] 6 equiv. of ArMgBr were used.

Scheme 2. Scope of Ni-catalyzed coupling with different arylsulfonic acids. *Reaction conditions:* 2.0 mmol $ArSO_3Na$, 6.0 mmol ArMgBr, 1 mol% $NiCl_2(PCy_3)_2$, THF, room temperature or 60 °C, 20 h. Isolated yields unless noted otherwise.



[a] GC assay yield *vs.* dodecane as internal standard.
[b] Product contained ~12% (*E*)-2-(prop-1-en-1-yl)naphthalene.
[c] i-PrMgCl was used.

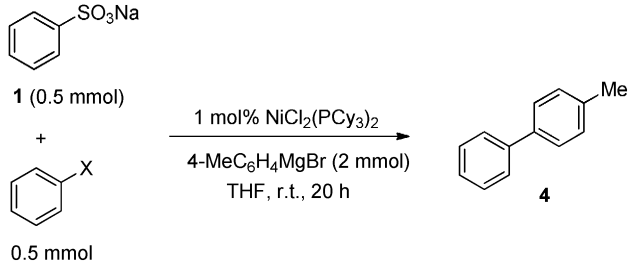
Scheme 3. Scope of Ni-catalyzed coupling with different alkyl Grignard reagents. *Reaction conditions:* 2.0 mmol $ArSO_3Na$, 6.0 mmol RMgX, 1 mol% $NiCl_2(PCy_3)_2$, THF, room temperature, 20 h. Isolated yields unless noted otherwise.



[a] GC assay yield *vs.* dodecane as internal standard.
[b] Reaction time of 48 h, 2 mol% catalyst.
[c] *i*-PrMgCl was used.

Scheme 4. Scope of Co-catalyzed coupling. *Reaction conditions:* 2.0 mmol $ArSO_3Na$, 6.0 mmol RMgBr, 1 mol% $CoCl_2(PCy_3)_2$, THF, 60 °C, 24 h. Isolated yields unless noted otherwise.

Table 2. Competition experiments with other electrophiles.[a]



Entry	PhX	Yield of **4** [%][b]	Unreacted **1** [%][b]	Unreacted PhX [%][b]
1	PhCl	97	5	0
2	PhBr	67	38	25
3	PhI	62	51	20
4	PhOTf	98	<2	0
5	PhSMe	65	17	37

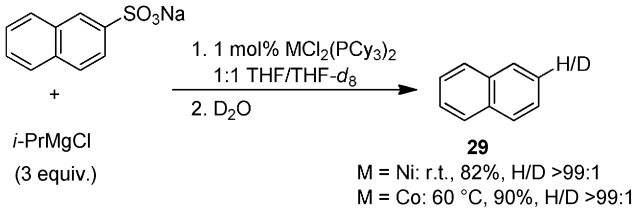
[a] *Reaction conditions:* 0.5 mmol **1**, 0.5 mmol PhX, 2.0 mmol 4-MeC_6H_4MgBr, 1 mol% $NiCl_2(PCy_3)_2$, THF, room temperature, 20 h.
[b] HPLC assay yields.

version of the arylsulfonate to product **28**, even when the reaction temperature was raised to 60 °C. The use of *i*-PrMgCl resulted in reduction to give **29** in 76% yield, thus providing a convenient method for reductive removal of the sulfonic acid moiety.[17]

The scope of the cross-coupling reaction was next explored using the cobalt catalyst $CoCl_2(PCy_3)_2$ (Scheme 4). Employing 1 mol% catalyst, the reaction proceeded at 60 °C to give biaryl products in good yields after 24 h (products **2**–**4** and **17**). The reaction was also amenable to the use of MeMgCl (product **22**) and reduction with *i*-PrMgCl (product **29**). The complex $CoCl_2(PCy_3)_2$ was first prepared in 1965[26] and has been used as a catalyst for butadiene polymerization.[27] To the best of our knowledge, this is the first use of this complex as an efficient catalyst for a cross-coupling reaction.

Competition experiments were conducted to examine the relative reactivity of different electrophiles compared to a sulfonic acid salt using $NiCl_2(PCy_3)_2$ as catalyst (Table 2). A 1:1 mixture of either PhCl, PhBr, PhI, PhOTf or PhSMe and $PhSO_3Na$ and 1 mol% $NiCl_2(PCy_3)_2$ in THF was treated at room temperature with 4-MeC_6H_4MgBr (4 equiv.). The reaction mixtures were allowed to stir at room temperature for 20 h, were quenched, and the crude product mixtures were analyzed by HPLC for assay yields of product **4** as well as of unreacted **1** and PhX. Based on the data, it can be concluded that the relative reactivity order of electrophiles under these reaction conditions is $PhOTf \approx PhCl > PhBr \approx PhI > PhSO_3Na > PhSMe$.

To probe whether the mechanism of the cross-coupling reaction proceeds through an oxidative addition



Scheme 5. Test for oxidative addition *versus* radical mechanism.

of Ni(0) to the Ar–S bond or by a radical/single electron transfer mechanism, we conducted the reaction of 2-naphthalenesulfonic acid sodium salt with *i*-PrMgCl in 1:1 THF/THF-d_8 (Scheme 5). The reaction was quenched upon complete conversion with D_2O. ^1H NMR and GC-MS analysis of the product showed <1% incorporation of deuterium. This suggests that the reaction proceeds by a traditional oxidative addition of Ni(0) into the Ar–S bond, followed by transmetallation of the isopropyl group, β-hydride elimination, and reductive elimination to give **29** and Ni(0). For a reaction proceeding through the intermediacy of radicals, H or D abstraction from the solvent would be expected to lead to significant D incorporation. These results are in concurrence with the findings of Snieckus and Milburn for the mechanism of the Kumada cross-coupling of arylsulfonamides.[17,28]

In conclusion, arylsulfonic acid salts have been demonstrated to be competent electrophiles in the nickel- or cobalt-catalyzed cross-coupling with Grignard reagents. Importantly, arylsulfonic acids are products of one of the oldest and most fundamental

methods of direct aromatic heterofunctionalization. Their utility as electrophiles in other cross-coupling reactions merits further exploration. While the nickel catalyst $NiCl_2(PCy_3)_2$ was shown to be optimal for the present reaction, the analogous cobalt catalyst $CoCl_2(PCy_3)_2$ was also shown to be effective at a higher temperature of 60 °C. The efficacy of $CoCl_2(PCy_3)_2$ as a catalyst for other cross-coupling reactions remains to be investigated.

Experimental Section

Typical Experimental Procedure (Compound 2)

An argon-purged flask equipped with a magnetic stir bar was charged with sodium arylsulfonate **1** (0.36 g, 2.0 mmol, 1.0 equiv.) and $NiCl_2(PCy_3)_2$ (13 mg, 1 mol%). The flask was sealed with a rubber septum, evacuated and filled with argon. THF (1.3 mL) was charged *via* a syringe. To this slurry, 4-methoxyphenylmagnesium bromide (12.0 mL, 0.5 M in THF, 3.0 equiv.) was added dropwise under argon. After the addition was complete, the reaction mixture was stirred at room temperature. After 20 h, HPLC analysis indicated complete consumption of sodium arylsulfonate **1**. The reaction mixture was cooled in an ice bath and quenched with saturated aqueous NH_4Cl (10 mL) and extracted with MTBE (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by chromatography on SiO_2 (hexanes) to provide **2** as a white solid; yield: 0.32 g (88%).

Procedures, spectral data, and copies of ^1H and ^{13}C NMR spectra are given in the Supporting Information.

Acknowledgements

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[22] In footnote #5 in ref.[6a], Wenkert noted that *p*-methylbiphenyl was detected in the reaction of 2-naphthyl tosylate with excess PhMgBr catalyzed by $NiCl_2(PPh_3)_2$. This indicates that the leaving group from the first coupling, *p*-TsOMgBr, underwent further reaction as an electrophile. To the best of our knowledge, this is the only prior report of a sulfonic acid salt undergoing cross-coupling with a Grignard reagent.
[23] The use of a lower stoichiometry of Grignard reagent generally resulted in incomplete conversion.
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