JOC Article

Nickel(0)-Catalyzed Cross-Coupling of Alkyl Arenesulfonates with Aryl Grignard Reagents

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The nickel-catalyzed cross-coupling reactions of neopentyl arenesulfonates with arylmagnesium bromides, involving nucleophilic aromatic substitution of alkyloxysulfonyl groups by aryl nucleophiles, take place in high yields. Optimal efficiencies are obtained by adding 3 + 2 equiv of the Grignard reagent to a mixture of dppfNiCl$_2$ and the sulfonate in refluxing THF. Neopentyl arenesulfonates are useful sources of the electrophilic aryl groups in these transition metal-catalyzed cross-coupling reactions. Aryl sulfonates are inappropriate due to their ambident reactivity under the reaction conditions. This new cross-coupling reaction can be used for the creative elimination of alkyloxysulfonyl groups from aromatic compounds and for the preparation of unsymmetric terphenyls and oligophenyls.

Introduction

Transition metal-promoted cross-coupling reactions of organometallic compounds with organic electrophiles rank among the most useful processes for forming carbon−carbon bonds.[1] Included in this family are the nickel- and palladium-catalyzed coupling of organic halides and pseudohalides, containing sp or sp^2 carbons at or immediately adjacent to the electrophilic center, with organoboronic acids,[2] organostannanes,[3] organozincs,[4] alkenes, alkynes,[5] and aryl Grignard reagents.[6] However, the use of group 10 transition metal complexes to promote the cross-coupling of unactivated sp^3 electrophiles has been less well explored. This could be due to the lack of reactivity of alkyl electrophiles[7] or to the formation of side products, such as olefins, by β-hydride elimination. Therefore, the development of a general coupling procedure, utilizing unactivated sp^3 electrophiles, has presented a challenge in the field of organic synthesis.[4c,8]

In a program directed at the development of a cross-coupling reaction utilizing alkyl electrophiles, we observed that 2,2-dimethyl-3-phenyl-1-propyl *p*-toluenesulfonate **1a** reacts with phenylmagnesium bromide **2a** in the presence of [1,1′-bis(diphenylphosphino)ferrocene]-dichloronickel(II) (dppfNiCl$_2$) in refluxing tetrahydrofuran (THF) to give 4-methylbiphenyl **3a** (Scheme 1). Since Wenkert and Takei observed that nickel(0) can insert into the sp^2 C−S bond of aryl or alkenyl sulfides and sulfones to yield nickel(II) complexes,[9] it has been known that alkylthio and alkylsulfonyl groups, directly bonded to arenes or alkenes, can be substituted for in nucleophilic aromatic substitution reactions with aryl and alkyl Grignard reagents in the presence of catalytic low-

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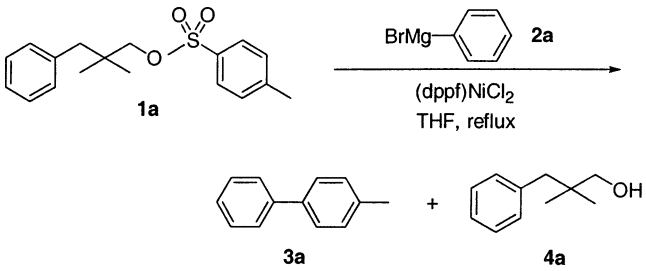
SCHEME 1



valent Ni species.[10] It was proposed that this process takes place through the common mechanism for transition metal-catalyzed cross-coupling reaction between organometallic reagents and organic electrophiles, involving sequential oxidative addition, transmetalation, and reductive elimination.[11]

It is interesting to note that neopentyl tosylate does not undergo a nickel-catalyzed nucleophilic substitution reaction with phenylmagnesioum bromide. In contrast, neopentyl iodides are known to react with arylmagnesium bromides[8a] and arylzincs[4c,12] in the presence of the same nickel catalyst to give neopentylarenes. Indeed, organic sulfonates have been especially valuable as electrophiles in transition metal-catalyzed cross-coupling reactions. Noteworthy are triflates, which participate in clean palladium- and nickel-catalyzed coupling reactions with organostannane,[13] boron,[14] aluminum,[15] magnesium,[16] and zinc[17] reagents. In addition, aryl mesylates are known to couple with nucleophiles in the presence of nickel catalysts,[18] and organic tosylates are reported to react with vinyltributylstannanes in the presence of a palladium catalyst.[19]

Our reactions present novel methods for the efficient and creative removal of alkyloxysulfonyl groups from aromatic compounds. Traditionally, sulfonyl groups are removed by using alkali metal[20] or Raney nickel[21] reduction, replacing the sulfur-containing group with a hydrogen atom, or simple reductive elimination,[22] leaving a residual double bond in the product. Our search for more constructive methods of manipulating sulfur-containing compounds is driven by the need to overcome the limitations of the above chemistry and to discover new synthetic procedures in such areas as solid-phase organic synthesis (SPOS). In addition, alkyl arenesulfonates could be useful electrophiles in transition metal-catalyzed cross-coupling reactions. While cross-coupling reactions are the accepted methods for preparation of unsymmetric biaryls, which are of great interest due to their biological properties,[23] these processes have largely relied on the use of organic halides and triflates as electrophiles.[1−6] The alkyloxysulfonyl group might be a suitable alternative to halides and triflates under some circumstances. For example, chemoselective sequential coupling of aromatic compounds that have both halogen and alkyloxysulfonyl groups would represent a practical approach to the preparation of unsymmetric terphenyls and oligophenyls, which have attracted much attention due to their optical[24] and electrical[25] properties.

In investigations aimed at probing the use of alkyloxysulfonylarenes in transition metal-catalyzed cross-coupling reactions, we have found that neopentyl arenesulfonates **1** undergo nickel(0)-catalyzed reactions with arylmagnesium bromides **2** to give the corresponding unsymmetric biaryls **3**. The results of this study are presented and discussed below.

Results and Discussion

In this study, the alkyl and aryl arenesulfonates **1** are prepared by employing a modification of literature pro-

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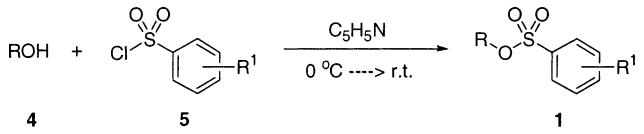
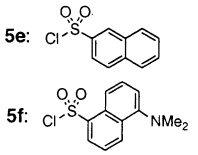
SCHEME 2



4 5 1

4a: R = 2,2-dimethyl-3-phenyl-1-propyl-
4b: R = 2,2-dimethylpropyl-
4c: R = 4-ethylphenyl-
4d: R = phenyl-

5a: R^1 = 4-Me
5b: R^1 = 4-^{t}Bu
5c: R^1 = 2,4,6-*tri*-Me
5d: R^1 = 4-OMe

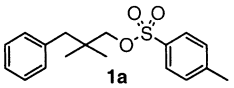
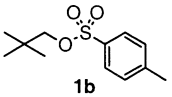
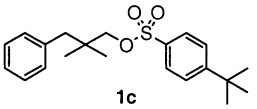
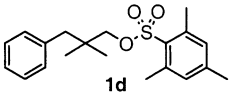
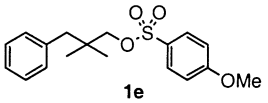
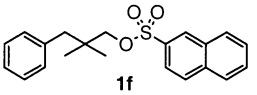
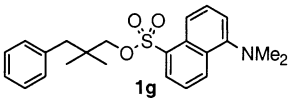
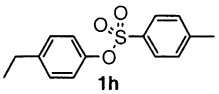
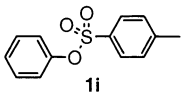


cedures (Scheme 2).[26] Two types of neopentyl moieties, 2,2-dimethyl-3-phenyl-1-propyl and 2,2-dimethyl-1-propyl, were selected as alkyl groups in these sulfonates to avoid competitive substitution and elimination of the arenesulfonate anions in reactions with Grignard reagents **2**. All sulfonates **1** were readily prepared in good yields (Table 1).

The cross-coupling reactions of **1a** with **2a** were investigated first in order to uncover optimum reaction conditions. A brief solvent survey indicated that reaction efficiencies are highest when THF is used as solvent and $dppfNiCl_2$ is used as catalyst (Table 2, entries 1−3). Three equivalents of Grignard reagents is insufficient to bring about complete reaction due to competitive self-dimerization (entry 4). However, when addition of the Grignard reagent is carried out in two portions, the overall yield increases. Specifically, addition of 3 equiv of **2a** initially and then 2 equiv after 12 h (denoted below as 3 + 2) leads to a higher yield as compared to a single addition of 5 equiv (entry 5). The reaction requires an elevated temperature to overcome the relatively low reactivity of **1a**. Reaction conducted at room temperature for 28 h leads to recovery of a significant amount of unreacted tosylate (entry 6). THF proved the best solvent when 1,2-[bis(diphenylphosphino)ethane]dichloronickel(II) ($dppeNiCl_2$) is used as catalyst (entries 7−9). However, the cross-coupling reaction proceeds in a higher yield in the presence of $dppfNiCl_2$ as compared to $dppeNiCl_2$ (compare entries 5 and 7−9). A nickel catalyst is required for the reaction to proceed. In the absence of catalyst, only a trace quantity of the product is formed (entry 10).

In these reactions, neopentyl alcohol **4a** is generated in the same quantity as the desired biaryl. This is presumably due to the evolution of sulfur dioxide from the departing neopentyloxysulfonyl anion. Even though no significant levels of byproducts originating from the neopentyl tosylate are observed, product purification is complicated by the fact that the crude reaction mixtures contain biphenyls derived by dimerization of **2a**. Thus, in anticipation of difficulties in isolating the products by preparative thin-layer chromatography, GC was used to determine yields included in Table 2. In summary, the optimization studies demonstrate that highest yields are obtained by using the 3 + 2 addition of **2a** to a mixture of $dppfNiCl_2$ and **1a** in refluxing THF. Unless otherwise stated, these reaction conditions were employed for the coupling reactions described below.

TABLE 1. Preparations of Alkyl and Aryl Arenesulfonates 1[a]

entry	alcohol **4**	sulfonyl chloride **5**	sulfonate **1**	yield (%)[b]
1	**4a**	**5a**	 **1a**	89
2	**4b**	**5a**	 **1b**	86
3	**4a**	**5b**	 **1c**	90
4	**4a**	**5c**	 **1d**	85
5	**4a**	**5d**	 **1e**	87
6	**4a**	**5e**	 **1f**	91
7	**4a**	**5f**	 **1g**	84
8	**4c**	**5a**	 **1h**	85
9	**4d**	**5a**	 **1i**	83

[a] Reactions of alcohols and phenols (5.52 mmol) with sulfonyl chlorides (5.25 mmol) were carried out in chloroform (12 mL) by using pyridine (10.50 mmol). [b] The yields refer to chromatographically isolated pure materials and based on compound **5**.

To establish a relative reactivity profile, reactions of aryl and vinyl Grignard reagents **2** with neopentyl tosylates **1a** and **1b**, promoted by 5 mol % of $dppfNiCl_2$ in refluxing THF, were probed (Scheme 3). Both 4-*tert*-butylphenylmagnesium bromide **2b** and 4-ethylphenylmagnesium bromide **2c** react with both tosylates to give the respective biaryl products **3b** and **3c** in high yields (Table 3, entries 1−4). On the other hand, the sterically hindered 2-ethylphenylmagnesium bromide **2d** reacts only slowly with **1a** and **1b** to give lower yields of the corresponding coupling products (entries 5 and 6). 4-Meth-

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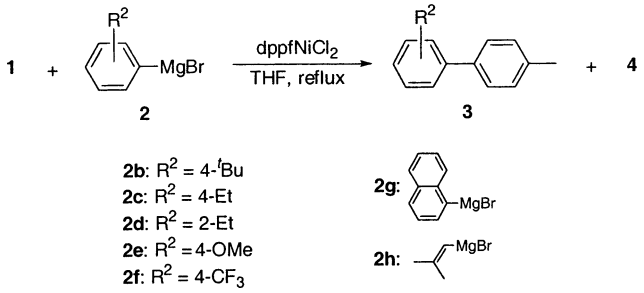
TABLE 2. Effect of Varying Reaction Conditions on the Coupling of 1a with 2a[a]

entry	**2a** (equiv)	catalyst[c]	solvent	*T*	time (h)	product **3a** yield (%)[f]
1	5	A[d]	Et_2O	reflux	26	82
2	5	A[d]	THF	reflux	24	92
3	5	A[d]	DME	reflux	30	84
4	3	A[d]	THF	reflux	24	72
5	3 + 2[b]	A[d]	THF	reflux	24	97
6	3 + 2[b]	A[d]	THF	rt	28	26
7	3 + 2[b]	B[e]	Et_2O	reflux	26	92
8	3 + 2[b]	B[e]	THF	reflux	24	93
9	3 + 2[b]	B[e]	DME	reflux	30	86
10	3 + 2[b]	none	THF	reflux	22	trace

[a] Reactions of **1a** (0.1 mmol) with **2a** (0.3−0.5 mmol) were carried out in the indicated solvent (3 mL) by using the indicated catalyst (0.005 mmol). [b] A mixture of **1a** (0.1 mmol), GC standard (0.1 mmol), and catalyst (0.005 mmol) in solvent (3 mL) was treated with 0.3 mmol of **2a** at the beginning of the reaction and an additional 0.2 mmol of **2a** after 12 h. [c] A: dppfNiCl$_2$. B: dppeNiCl$_2$. [d] Resulting in a color change from dark green to dark brown after the addition of Grignard reagent. [e] Resulting in a color change from reddish brown to dark brown after the addition of Grignard reagent. [f] GC yields are based on the amount of **1a**.

SCHEME 3

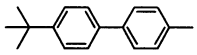
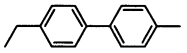
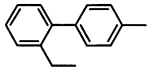
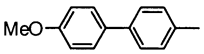
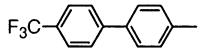
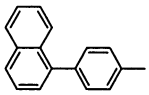
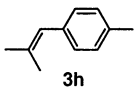


oxyphenylmagnesium bromide **2e** undergoes cross-coupling with **1a** and **1b** in slightly lower yields, owing to competitive insertion of the nickel catalyst into the carbon−oxygen bond of the product (entries 7 and 8).[27] 4-Trifluoromethylphenylmagnesium bromide **2f**, which has a strong electron-withdrawing aryl substituent, does not react with the tosylates under the reaction conditions employed (entries 9 and 10). Finally, 1-naphthyl Grignard reagent **2g** reacts efficiently with both tosylates (entries 11 and 12), while vinylmagnesium bromide **2h** reacts exceptionally slowly to form the vinylarene **3h** in moderate yields (entries 13 and 14).

The reactivity profile developed above indicates that most arylmagnesium bromides **2** react with **1a** and **1b** in high yields, while sterically hindered aryl and vinyl Grignard reagents display reduced reactivity and an electron-deficient nucleophile is unreactive. It should be noted that **3b** requires preparative HPLC for their separation from another biphenyl, simultaneously formed by self-coupling of the arylmagnesium bromide, while **3e** and **3g** can be purified by column chromatography and preparative thin-layer chromatography, respectively. Even though **1a** and **1b** generally have similar reactivities with aryl Grignard reagents, the tosylate **1a** bearing the 2,2-dimethyl-3-phenyl-1-propyl group is particularly attractive, since it displays slightly higher reactivity especially in cross-coupling reactions with less reactive nucleophiles (entries 5, 6, 13, and 14). Therefore, it was employed as an alkyl group of arenesulfonates **1** for the coupling reactions described below.

(27) (a) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, 2246−2247. (b) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915−3918. (c) Johnstone, R. A. W.; McLean, W. N. *Tetrahedron Lett.* **1988**, *29*, 5553−5556.

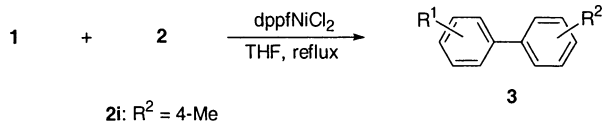
TABLE 3. Nickel-Catalyzed Coupling of Neopentyl Tosylates 1a and 1b with 2a[a]

entry	tosylate **1**	Grignard reagent **2**	time (h)	product **3**	yield (%)[b]
1	**1a**	**2b**	28	 **3b**	84
2	**1b**	**2b**	28	**3b**	87
3	**1a**	**2c**	25	 **3c**	93[c]
4	**1b**	**2c**	25	**3c**	95[c]
5	**1a**	**2d**	52	 **3d**	73[c]
6	**1b**	**2d**	52	**3d**	62[c]
7	**1a**	**2e**	28	 **3e**	78
8	**1b**	**2e**	28	**3e**	72
9	**1a**	**2f**	28	 **3f**	-
10	**1b**	**2f**	28	**3f**	-
11	**1a**	**2g**	32	 **3g**	74
12	**1b**	**2g**	32	**3g**	73
13	**1a**	**2h**	55	 **3h**	53[c]
14	**1b**	**2h**	55	**3h**	43[c]

[a] Reactions of tosylate **1a** and **1b** (0.1 mmol) with **2** (0.3 + 0.2 mmol) were carried out at the refluxing temperature of THF (3 mL) by using dppfNiCl$_2$ (0.005 mmol). [b] The yields refer to chromatographically isolated pure materials and based on **1a** or **1b**. [c] GC yield based on **1a** or **1b**.

The results of cross-coupling reactions between various **1** and Grignard reagents **2** (Scheme 4), performed in the presence of 5 mol % of dppfNiCl$_2$ in refluxing THF, are summarized in Table 4. Most of these processes proceed in moderate to high yields to give the corresponding biaryls **3**. 2,2-Dimethyl-3-phenyl-1-propyl 4-*tert*-butylbenzenesulfonate **1c** reacts with both phenyl- (**2a**) and

SCHEME 4



p-tolylmagnesium bromide (**2i**) to generate 4-*tert*-butylbiphenyl **3i** and 4-*tert*-butyl-4′-methylbiphenyl **3b**, respectively, in good yields (entries 1 and 2). While the remote bulky substituent, 4-*tert*-butyl, does not decrease the reactivity of arenesulfonate **1c**, the two closely located *o*-methyl groups of 1,3,5-trimethylbenzenesulfonate **1d** seriously hinder the progress of the nickel-catalyzed oxidative addition reaction. Accordingly, reactions of **1d** with **2a** and **2i** afford the corresponding biphenyls, **3j** and **3l**, in low yields; more than 40% of **1d** remains unreacted after 2 d (entries 3 and 5). Only **2b** reacts with this sterically hindered sulfonate to generate the product **3k** in moderate yield (entry 4).

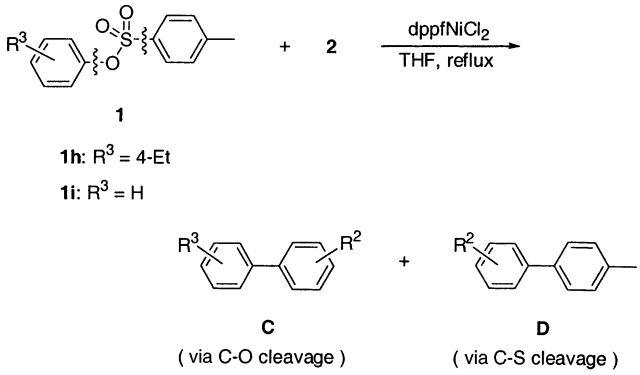
4-Methoxybenzenesulfonate **1e** is reactive with **2a**, **2b**, and **2i**, and the resulting methoxybiphenyls **3m**, **3n**, and **3e** are obtained in yields ranging from 58 to 62%. The diminished efficiencies of these processes are attributed to secondary cross-coupling reactions of the initially formed methoxybiphenyls with excess Grignard reagents via cleavage of carbon−oxygen bonds.[27] The secondary reactions produce the symmetric terphenyls, *p*-terphenyl **6a**, 4,4′-di-*tert*-butylterphenyl **6b**, and 4,4′-dimethylterphenyl **6c**, respectively (entries 6−8).

2,2-Dimethyl-3-phenyl-1-propyl 2-naphthalenesulfonate **1f** reacts with **2a**, **2b**, and **2i** to give biaryls **3o**, **3p**, and **3q** in good yields (entries 9−11). The coupling reaction of 5-(dimethylamino)-1-naphthalenesulfonate **1g** with these aryl Grignard reagents also efficiently produces the corresponding aminobiaryls **3r**, **3s**, and **3t** (entries 12−14). Products arising by cleavage of the C−N bond are not detected in the reaction mixtures. Naphthalenesulfonates **1f** and **1g** show higher reactivity than other benzenesulfonates in these reactions. Generally, the more highly conjugated arenesulfonates undergo coupling with Grignard reagents more rapidly under the reaction conditions described above. The results, summarized in Table 4, show that alkyl arenesulfonates are useful sources of various electrophilic aryl groups for transition metal-catalyzed coupling reactions.

The issue of relative rates of C−S bond vs C−O bond cleavage under the nickel-catalyzed cross-coupling conditions was also explored in this effort. It is well-known that oxidative addition of group 10 transition metals to unactivated sp^3 carbon−heteroatom bonds is slower than to sp^2 carbon−heteroatom bonds.[1−7] Therefore, to eliminate the hybridization effect, cross-coupling reactions of 4-ethylphenyl *p*-toluenesulfonate **1h** and phenyl *p*-toluenesulfonate **1i**, both having oxygen and sulfur atoms bonded to arene groups, with **2** were investigated (Scheme 5).

Two different biaryls are formed in coupling reactions of the aryl tosylates **1h** and **1i** with **2** (Table 5). Reactions of **1h** with **2a** and **2b** produce biphenyls **3a** and **3b**, via cleavage of the C−S bond, in greater yields than **3u** and **3v**, produced by C−O bond cleavage (entries 1 and 2). The more electron-rich nucleophile **2b** displays reduced selectivity. Also, an electron-donating substituent on the

SCHEME 5



aryloxy group decreases the C−O bond-cleavage reactivity. When the ethyl group of **1h** is substituted by hydrogen, the reactivity of the C−O bond in the resulting aryl tosylate **1i** is increased (entry 3). This reduces the ratio of product obtained by C−S vs C−O cleavage. These results show that the aryloxysulfonyl group is more labile than tosylate under the standard reaction conditions. This leads to the proposal that aryl arenesulfonates are not promising electrophiles for selective cross-couplings with arylmagnesium bromides in the presence of nickel catalyst.

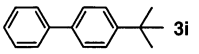
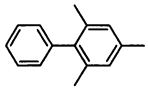
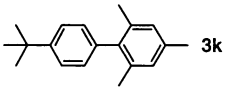
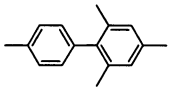
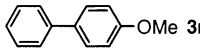
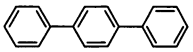
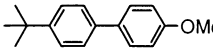
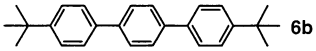
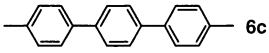
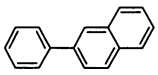
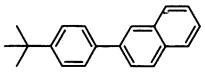
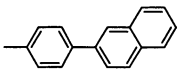
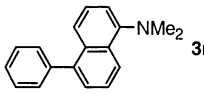
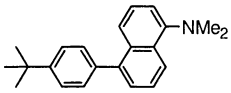
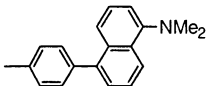
Conclusion

To our knowledge, the study reported above is the first general exploration of transition metal-catalyzed cross-coupling reactions of alkyloxysulfonyl arenes with nucleophiles. In this effort, we have observed that unsymmetric biaryls **3** can be prepared in high yields by the nickel(0)-catalyzed cross-coupling of alkyl arenesulfonates **1** with aryl Grignard reagents **2**. The highest yields are obtained by adding 3 + 2 equiv of **2** to a mixture of $dppfNiCl_2$ and **1** in refluxing THF. It appears that this process will comprise a novel and creative method for removal of alkyloxysulfonyl groups from aromatic compounds. Moreover, alkyloxysulfonyl arenes **1** are expected to be excellent electrophiles for nickel-catalyzed cross-coupling reactions. This is especially true in the context of the preparation of unsymmetric terphenyls and oligophenyls, where chemoselective sequential coupling of aromatic compounds that contain both halogens and an alkyloxysulfonyl groups would serve as an ideal strategy.

Experimental Section

All reactions were carried out under an inert atmosphere of N_2 or Ar. Solvents were distilled from an appropriate drying agent prior to use: THF and DME from sodium−benzophenone ketyl, and Et_2O from calcium hydride. Pyridine was dried over CaH_2 and distilled. Commercially available reagents were used without further purification unless otherwise stated. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were registered in $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard, unless otherwise stated. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.2 ppm. All coupling constants, *J*, are reported in hertz (Hz). Column chromatography was performed on silica gel 60, 70−230 mesh. Analytical thin-layer chromatography (TLC) was performed using Merck Kieselgel 60 F_{254} precoated plates (0.25 mm) with a fluorescent indicator and visualized

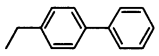
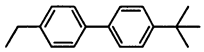
TABLE 4. Nickel-Catalyzed Coupling of Neopentyl Arenesulfonates 1 with 2[a]

entry	sulfonate 1	Grignard reagent 2	time (h)	product 3 (6)	yield (%)[b]
1	**1c**	**2a**	26	 **3i**	83
2	**1c**	**2i**	26	**3b**	78
3	**1d**	**2a**	48	 **3j**	34[c]
4	**1d**	**2b**	48	 **3k**	56[c]
5	**1d**	**2i**	48	 **3l**	27[c]
6	**1e**	**2a**	28	 OMe **3m**	62
				 **6a**	7.3[c]
7	**1e**	**2b**	28	 OMe **3n**	58
				 **6b**	20.4[c]
8	**1e**	**2i**	28	**3e**	60
				 **6c**	18.3[c]
9	**1f**	**2a**	24	 **3o**	78.5
10	**1f**	**2b**	24	 **3p**	83
11	**1f**	**2i**	24	 **3q**	81
12	**1g**	**2a**	28	 NMe_2 **3r**	68
13	**1g**	**2b**	26	 NMe_2 **3s**	76.5
14	**1g**	**2i**	26	 NMe_2 **3t**	71

[a] Reactions of sulfonates **1** (0.1 mmol) with **2** (0.3 + 0.2 mmol) were carried out at the refluxing temperature of THF (3 mL) using dppfNiCl$_2$ (0.005 mmol). [b] The yields refer to chromatographically isolated pure materials and based on **1**. [c] GC yield based on **1**.

with UV light (254 and 365 nm) or by iodine vapor staining. Preparative TLC was carried out on 20 × 20 cm glass plates coated with Aldrich silica gel (1 mm thick). Analytical and preparative HPLC was performed with an instrument equipped with a UV detector set at 254 nm. Octadecylsilane-coated columns, 4.6 × 250 mm or 20 × 250 mm, with 5 or 10 μm particle size were used for analytical or preparative runs, respectively. A flow rate of 0.8 or 5 mL/min was used. GC analysis was performed on a bonded 5% phenylpolysiloxane BPX 5 capillary column (SGE, 30 m, 0.32 mm i.d.). Electron impact (EI, 70 eV) was used as the ionization method for the mass spectrometry. Main fragmentation peaks are reported with their relative intensities (percent values are in parentheses). Mass data are reported in mass units (*m*/*z*). Melting points were obtained and are uncorrected. DppfNiCl$_2$ was prepared according to a literature procedure.[28] [mp 282−283

TABLE 5. Nickel-Catalyzed Coupling of Aryl Tosylates 1h and 1i with 2[a]

entry	tosylate 1	Grignard reagent 2	time (h)	product C	product D	yield (%)[b]	(C : D)[c]
1	**1h**	**2a**	28	 **3u**	**3a**	73	(1.0 : 11.2)
2	**1h**	**2b**	28	 **3v**	**3b**	83	(1.0 : 7.2)
3	**1i**	**2b**	26	**3i**	**3b**	81	(1.0 : 2.9)

[a] Reactions of tosylate **1h** and **1i** (0.1 mmol) with **2** (0.3 mmol) were carried out at the refluxing temperature of THF (3 mL) using dppfNiCl$_2$ (0.005 mmol). [b] GC yields based on **1h** or **1i**. Yields were not optimized. [c] The ratios of compounds C and D as determined by GC are in parentheses.

°C (lit. mp 283−284 °C)]. DppeNiCl$_2$ and phenyl- (**2a**) (1.0 M, THF), 4-*tert*-butylphenyl- (**2b**) (2.0 M, Et$_2$O), 4-trifluorophenyl- (**2f**) (1.0 M, THF), and *p*-tolylmagnesium bromide (**2i**) (1.0 M, Et$_2$O) were purchased and used as received. 4-Ethylphenyl- (**2c**), 2-ethylphenyl- (**2d**), 4-methoxyphenyl- (**2e**), 1-naphthyl- (**2g**), and isobutenylmagnesium bromide (**2h**) were prepared by reacting magnesium turnings with the appropriate organic halide in THF.

General Procedure for the Preparation of Sulfonates 1. To the alcohol or phenol **4** (5.52 mmol) in chloroform (12 mL) at 0 °C were added pyridine (0.85 mL, 10.50 mmol) dropwise over a period of 20 min and sulfonyl chloride **5** (5.25 mmol) in small portions. This reaction mixture was stirred at room temperature for 12 h and diluted with Et$_2$O and then 0.1% aqueous HCl. The separated organic layer was washed with 0.1% aqueous HCl, water, and saturated aqueous NaCl; dried over MgSO$_4$; and concentrated in vacuo. The crude sulfonates **1** were purified by either column chromatography or by recrystallization.

2,2-Dimethyl-3-phenyl-1-propyl *p*-toluenesulfonate (1a) was prepared by the reaction of **4a** (0.91 g, 5.52 mmol) with **5a** (1.00 g, 5.25 mmol). The crude compound was purified by column chromatography (ethyl acetate:*n*-hexane = 1:4) to afford **1a** (1.47 g, 89%) as a colorless oil that solidified upon standing to a white solid: mp 71−72 °C (lit.[29a] mp 71.4−71.8 °C, lit.[29b] mp 71.4−71.9 °C); TLC R_f (Et$_2$O:*n*-hexane = 1:4) 0.38; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.86 (s, 6H), 2.45 (s, 3H), 2.54 (s, 2H), 3.65 (s, 2H), 6.99−7.04 (m, 2H), 7.16−7.26 (m, 3H), 7.35 (d, J = 8.23 Hz, 2H), 7.81 (d, J = 8.23 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.7, 24.0 (×2), 35.3, 44.3, 77.2, 126.5, 128.1 (×2), 128.2 (×2), 130.1 (×2), 130.7 (×2), 133.2, 137.6, 145.0; LRMS (EI) *m*/*z* (rel abundance) 318 (M$^+$, 22), 187 (63), 155 (54), 107 (6), 91 (81), 70 (21), 65 (30), 57 (100).

2,2-Dimethyl-1-propyl *p*-toluenesulfonate (1b) was prepared by the reaction of **4b** (0.49 g, 5.52 mmol) with **5a** (1.00 g, 5.25 mmol). The crude compound was purified by column chromatography (ethyl acetate:*n*-hexane = 1:4) to afford **1b** (1.09 g, 86%) as a colorless oil that solidified upon standing to a white solid: mp 46 °C (lit.[30] mp 48 °C); TLC R_f (Et$_2$O:*n*-hexane = 1:4) 0.22; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.90 (s, 9H), 2.45 (s, 3H), 3.66 (s, 2H), 7.35 (d, J = 8.22 Hz, 2H), 7.79 (d, J = 8.22 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.7, 26.1 (×3), 31.7, 79.6, 128.1 (×2), 130.0 (×2), 133.3, 144.9; LRMS (EI) *m*/*z* (rel abundance) 242 (M$^+$, 3%).

2,2-Dimethyl-3-phenyl-1-propyl *p*-*tert*-butylbenzenesulfonate (1c) was prepared by the reaction of **4a** (0.91 g, 5.52 mmol) with **5b** (1.22 g, 5.25 mmol). The crude compound was purified by recrystallization from cyclohexane to give **1c** (1.70 g, 90%) as a white crystalline solid: mp 103−103.5 °C (uncorrected); TLC R_f 0.46 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.88 (s, 6H), 1.37 (s, 9H), 2.55 (s, 2H), 3.67 (s, 2H), 6.99−7.03 (m, 2H), 7.14−7.21 (m, 3H), 7.57 (d, J = 8.73 Hz, 2H), 7.85 (d, J = 8.73 Hz, 2H); ^{13}C NMR (75 MHz, acetone-d_6) δ 24.2 (×2), 31.3 (×3), 35.8, 35.9, 44.8, 77.8, 127.2, 127.5 (×2), 128.8 (×2), 128.9 (×2), 131.4 (×2), 134.4, 138.6, 158.8; HRMS (EI, 70 eV) calcd for C$_{21}$H$_{28}$O$_3$S (M$^+$) 360.1759, found 360.1432.

2,2-Dimethyl-3-phenyl-1-propyl 2,4,6-trimethylbenzenesulfonate (1d) was prepared by the reaction of **4a** (0.91 g, 5.52 mmol) with **5c** (1.15 g, 5.25 mmol). The crude compound was purified by column chromatography (ethyl acetate:*n*-hexane = 1:4) to afford **1d** (1.54 g, 85%) as a colorless oil that solidified upon standing to a white solid: mp 43.5−45 °C (uncorrected); TLC R_f 0.48 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.89 (s, 6H), 2.33 (s, 3H), 2.57 (s, 2H), 2.66 (s, 6H), 3.63 (s, 2H), 6.99 (s, 2H), 7.05−7.08 (m, 2H), 7.20−7.27 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.1, 22.8 (×2), 24.2 (×2), 35.3, 44.6, 76.6, 126.6, 128.2 (×2), 130.8 (×2), 131.0 (×2), 132.0 (×2), 137.7, 140.2, 143.5; HRMS (EI, 70 eV) calcd for C$_{20}$H$_{26}$O$_3$S (M$^+$) 346.1603, found 346.1603.

2,2-Dimethyl-3-phenyl-1-propyl *p*-methoxybenzenesulfonate (1e) was prepared by the reaction of **4a** (0.91 g, 5.52 mmol) with **5d** (1.08 g, 5.25 mmol). The crude compound was purified by column chromatography (ethyl acetate:*n*-hexane = 1:8) to afford **1e** (1.53 g, 87%) as a colorless oil that solidified upon standing to a white solid: mp 85 °C (uncorrected); TLC R_f 0.26 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.86 (s, 6H), 2.54 (s, 2H), 3.64 (s, 2H), 3.89 (s, 3H), 7.02 (d, J = 9.06 Hz, 2H), 7.15−7.24 (m, 2H), 7.17−7.23 (m, 3H), 7.86 (d, J = 9.06 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 24.1 (×2), 35.3, 44.3, 55.8, 77.0, 114.6 (×2), 126.5, 127.6, 128.2 (×2), 130.4 (×2), 130.7 (×2), 137.7, 164.018; HRMS (EI, 70 eV) calcd for C$_{18}$H$_{22}$O$_4$S (M+) 334.1239, found 334.1234.

2,2-Dimethyl-3-phenyl-1-propyl 2-naphthylenesulfonate (1f) was prepared by the reaction of **4a** (0.91 g, 5.52 mmol) with **5e** (1.19 g, 5.25 mmol). The crude compound was purified by recrystallization from cyclohexane to give **1f** (1.69 g, 91%) as a white crystalline solid: mp 86−87 °C (uncorrected); TLC R_f 0.36 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.87 (s, 6H), 2.55 (s, 2H), 3.71 (s, 2H), 6.98−7.01 (m, 2H), 7.11−7.14 (m, 3H), 7.64−7.75 (m, 2H), 7.89−8.05 (m, 4H), 8.52 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 23.9 (×2), 35.2, 44.2, 77.4, 122.7, 126.4, 127.9, 128.0 (×2), 128.1, 129.5, 129.5, 129.8, 129.9, 130.5 (×2), 132.1, 132.9, 135.4, 137.4; HRMS (EI, 70 eV) calcd for C$_{21}$H$_{22}$O$_3$S (M$^+$) 354.1290, found 354.1275.

2,2-Dimethyl-3-phenyl-1-propyl 5-(dimethylamino)-1-naphthalenesulfonate (1 g) was prepared by the reaction of **4a** (0.64 g, 3.91 mmol) with **5f** (1.00 g, 3.70 mmol). The crude

(28) Rudie, A. W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859−2863.
(29) (a) Warrick, Jr., P.; Saunders, Jr., W. H. *J. Am. Chem. Soc.* **1962**, *84*, 4095−4100. (b) Owen, J. R.; Saunders, Jr., W. H. *J. Am. Chem. Soc.* **1966**, *88*, 5809−5816.
(30) Yousefzadeh, P.; Mann, C. K. *J. Org. Chem.* **2001**, *66*, 6432−6439.

compound was purified by column chromatography (ethyl acetate:*n*-hexane = 1:10) to give **1g** (1.23 g, 84%) a fluorescent yellowish oil: TLC R_f 0.36 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (s, 6H), 2.52 (s, 2H), 2.89 (s, 6H), 3.62 (s, 2H), 6.94−6.97 (m, 2H), 7.10−7.15 (m, 3H), 7.22 (dd, J = 7.56, 0.67 Hz, 1H), 7.54 (dd, J = 8.56, 7.38 Hz, 1H), 7.62 (dd, J = 8.73, 7.56 Hz, 1H), 8.27 (dd, J = 7.38, 1.17 Hz, 1H), 8.38 (dt, J = 8.73, 0.67 Hz, 1H), 8.62 (dt, J = 8.56, 1.17 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1 (2C), 35.3 (1C), 44.3 (1C), 45.5 (2C), 77.6 (1C), 115.8 (1C), 119.9 (1C), 123.3 (1C), 126.1 (1C), 126.4 (1C), 128.1 (2C), 128.9 (1C), 130.1 (1C), 130.6 (2C), 131.6 (1C), 137.6 (1C), 139.0 (1C), 152.1 (1C); HRMS (EI, 70 eV) calcd for $C_{23}H_{27}NO_3S$ (M^+) 397.1712, found 397.1298.

4-Ethylphenyl *p*-toluenesulfonate (1h) was prepared by the reaction of **4c** (0.67 g, 5.52 mmol) with **5a** (1.00 g, 5.25 mmol). The crude compound was purified by column chromatography (ethyl acetate:*n*-hexane = 1:8) to afford **1h** (1.23 g, 85%) as a colorless oil that solidified upon standing to a white solid: mp 65 °C (uncorrected); TLC R_f 0.28 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, J = 7.63 Hz, 3H), 2.44 (s, 3H), 2.60 (q, J = 7.63 Hz, 2H), 6.88 (d, J = 8.56 Hz, 2H), 7.09 (d, J = 8.56 Hz, 2H), 7.30 (d, J = 8.22 Hz, 2H), 7.70 (d, J = 8.22 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 21.7, 28.2, 122.3 (×2), 128.7 (×2), 129.1 (×2), 129.9 (×2), 132.8, 143.4, 145.5, 147.9; LRMS *m*/*z* (rel abundance) 276 (M^+, 85), 197 (5.5), 155 (100), 139 (4.5), 121 (52), 91 (81), 77 (16), 65 (12.5).

Phenyl *p*-toluenesulfonate (1i) was prepared by the reaction of **4d** (0.49 mL, 5.52 mmol) with **5a** (1.00 g, 5.25 mmol). The crude compound was purified by recrystallization from *n*-hexane to give **1i** (1.08 g, 83%) as a white needle crystal: mp 93−94 °C (uncorrected); TLC R_f 0.18 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, acetone-d_6) δ 2.44 (s, 3H), 7.02−7.06 (m, 2H), 7.23−7.33 (m, 5H), 7.70 (d, J = 8.39 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 122.6 (×2), 127.3, 128.8 (×2), 129.9 (×2), 130.0 (×2), 132.8, 145.6, 150.0; LRMS *m*/*z* (rel abundance) 248 (M^+, 32), 207 (8), 155 (55), 91 (100), 65 (35).

General Procedure for Cross-Coupling Reaction. To a stirred solution of sulfonate **1** (0.1 mmol) and nickel catalyst (0.005 mmol) in dry THF (3 mL) was added aryl Grignard reagents **2** (0.3 mmol) via syringe at room temperature. This resulted in a color change from dark green to dark brown in the case of $dppfNiCl_2$ and from reddish brown to dark brown for $dppeNiCl_2$. The reaction mixture was heated at reflux for 12 h, cooled to room temperature, and an additional 0.2 mmol of **2** was added to the solution. The resulting mixture was heated at reflux for 10 h, cooled to room temperature, and diluted with Et_2O and 1% aqueous HCl. The separated organic layer was washed with a 1% aqueous HCl, water, and brine; dried over $MgSO_4$; and concentrated in vacuo. The product **3** was purified by chromatography.

Nickel-Catalyzed Coupling of Neopentyl Tosylates 1a and 1b with Arylmagnesium Bromides 2.

4-Methyl-4′-*tert*-butylbiphenyl (3b) was prepared by the reaction of **1a** (31.84 mg, 0.1 mmol) or **1b** (24.23 mg, 0.1 mmol) with **2b** (2.0 M in Et_2O, 0.15 mL, 0.3 mmol + 0.1 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3b** (18.84 mg, 84% or 19.52 mg, 87%) as a white solid: mp 75−76 °C (uncorrected); TLC R_f 0.66 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 2.39 (s, 3H), 7.24 (d, J = 8.48 Hz, 2H), 7.45 (d, J = 8.73 Hz, 2H), 7.49 (d, J = 8.48 Hz, 2H), 7.53 (d, J = 8.73 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 31.5 (×3), 34.6, 125.9 (×2), 126.9 (×2), 127.1 (×2), 129.7 (×2), 137.0, 138.5, 138.6, 150.2; HRMS (EI, 70 eV) calcd for $C_{17}H_{20}$ (M^+), 224.1565, found 224.1546.

4-Methyl-4′-methoxybiphenyl (3e) was prepared by the reaction of **1a** (31.84 mg, 0.1 mmol) or **1b** (24.23 mg, 0.1 mmol) with **2e** (0.5 M in THF, 0.6 mL, 0.3 mmol + 0.4 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The crude compound was purified by column chromatography (Et_2O: *n*-hexane = 1:4) to give **3e** (15.46 mg, 78% or 14.27 mg, 72%) as a white solid: mp 102−104 °C (lit.[31a] mp 107 °C, lit.[31b] mp 108 °C); TLC R_f 0.49 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.84 (s, 3H), 6.96 (d, J = 8.90 Hz, 2H), 7.22 (d, J = 8.40 Hz, 2H), 7.45 (d, J = 8.40 Hz, 2H), 7.51 (d, J = 8.90 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 55.435, 114.4 (×2), 126.8 (×2), 128.2 (×2), 129.7 (×2), 134.0, 136.6, 138.3, 159.3; HRMS (EI, 70 eV) calcd for $C_{14}H_{14}O$ (M^+), 198.1045, found 198.1024.

1-(4-Tolyl)naphthalene (3g) was prepared by the reaction of **1a** (31.84 mg, 0.1 mmol) or **1b** (24.23 mg, 0.1 mmol) with **2g** (0.5 M in THF, 0.6 mL, 0.3 mmol + 0.4 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3g** (16.15 mg, 74% or 15.94 mg, 73%) as a pale yellowish oil: TLC R_f 0.58 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.30 (d, J = Hz, 2H), 7.39−7.55 (m, 6H), 7.83−7.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 125.7, 126.0, 126.2, 126.4, 127.2, 127.7, 128.5, 129.2 (×2), 130.2 (×2), 132.0, 134.1, 137.2, 138.1, 140.5; HRMS (EI, 70 eV) calcd for $C_{17}H_{14}$ (M^+), 218.1096, found 218.1062.

Nickel-Catalyzed Coupling of Neopentyl Arenesulfonates 1 with Arylmagnesium Bromides 2.

4-*tert*-Butylbiphenyl (3i) was prepared by the reaction of **1c** (36.05 mg, 0.1 mmol) with **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3i** (17.46 mg, 83%) as a white solid: mp 46−47 °C (uncorrected); TLC R_f 0.64 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 7.32 (t, J = 7.30 Hz, 1H), 7.39−7.49 (m, 4H), 7.52−7.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5 (×3), 34.6, 126.0 (×2), 127.1 (×2), 127.2, 127.3 (×2), 129.0 (×2), 138.6, 141.4, 150.6; HRMS (EI, 70 eV) calcd for $C_{16}H_{18}$ (M^+), 210.1409, found 210.1405.

4-Methyl-4′-*tert*-butylbiphenyl (3b) was prepared by the reaction of **1c** (36.05 mg, 0.1 mmol) with **2i** (1.0 M in Et_2O, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The crude compound was purified by preparative HPLC (CH_3CN) to give **3b** (16.41 mg, 78%) as a white solid.

4-Methoxybiphenyl (3m) was prepared by the reaction of **1e** (33.4 mg, 0.1 mmol) with **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The reaction mixture contained **3m** (73.5%) and **6a** (7.3%) by GC and GC−MS analysis. The crude compound was purified by preparative TLC (*n*-hexane) to give **3m** (11.42 mg, 62%) as a white solid: mp 88−89 °C [an authentic sample[32a] (mp 86−90 °C)]; This material gave ^{1}H and ^{13}C NMR spectra identical to literature data.[32b]

4-*tert*-Butyl-4′-methoxybiphenyl (3n) was prepared by the reaction of **1e** (33.45 mg, 0.1 mmol) with **2b** (2.0 M in Et_2O, 0.15 mL, 0.3 mmol + 0.1 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The reaction mixture contained **3n** (69.5%) and **6b** (20.4%) by GC and GC−MS analysis. The crude compound was purified by column chromatography (Et_2O:*n*-hexane = 1:4) to give **3n** (13.94 mg, 58%) as a white solid: mp 127−128 °C (uncorrected); TLC R_f 0.52 (Et_2O:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.84 (s, 3H), 6.97 (2H, J = 8.9 Hz, 2H), 7.44 (2H, J = 8.73 Hz, 2H), 7.50 (2H, J = 8.73 Hz, 2H); 7.53 (2H, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5, 34.6 (×3), 55.4, 114.3 (×2), 125.9 (×2), 126.6 (×2), 128.3 (×2), 133.9, 138.2, 149.9, 159.3; HRMS (EI, 70 eV) calcd for $C_{17}H_{20}O$ (M^+), 240.1514, found 240.1510.

4-Methyl-4′-methoxybiphenyl (3e) was prepared by the reaction of **1e** (33.44 mg, 0.1 mmol) with **2i** (1.0 M in Et_2O, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of $dppfNiCl_2$. The reaction mixture contained **3e** (68.8%) and **6c** (18.3%) by GC and GC−MS analysis. The crude compound was

(31) (a). Lourak, M, Vanderesse, R, Fort, Y, Caubere, P. *J. Org. Chem.* **1989**, *54*, 4844−4848. (b). Tamura, Y.; Chun, M. W.; Inoue, K.; Minamikawa, J. *Synthesis* **1978**, *11*, 822.

(32) (a) An authentic sample of 4-methoxybiphenyl was purchased from Aldrich Chemical Co. (b) Trost, B. M.; Arndt, H. C. *J. Am. Chem. Soc.* **1973**, *95* (16), 5288−5298.

purified by column chromatography (Et_2O:*n*-hexane = 1:4) to give **3e** (11.89 mg, 60%) as a white solid:

2-Phenylnaphthalene (3o) was prepared by the reaction of **1f** (35.45 mg, 0.1 mmol) with **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3o** (16.04 mg, 78.5%) as a white solid: mp 108−109 °C (lit.[33] mp 108−109 °C); TLC R_f 0.56 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.42 (m, 1H), 7.43−7.53 (m, 4H), 7.69−7.77 (m, 3H), 7.82−7.93 (m, 3H), 8.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.9, 126.1, 126.2, 126.6, 127.6, 127.7 (×2), 127.9, 128.5, 128.7, 129.1 (×2), 132.9, 134.0, 138.9, 141.4; HRMS (EI, 70 eV) calcd for $C_{16}H_{12}$ (M^+), 204.0939, found 204.0917.

2-(4-*tert*-Butylphenyl)naphthalene (3p) was prepared by the reaction of **1f** (35.45 mg, 0.1 mmol) with **2b** (2.0 M in Et_2O, 0.15 mL, 0.3 mmol + 0.1 mL, 0.2 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3p** (21.61 mg, 83%) as a pale yellowish solid: mp 104−106 °C (uncorrected); TLC R_f 0.64 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 9H), 7.49−7.54 (m, 4H), 7.69 (d, J = 8.73 Hz, 2H), 7.77 (d, J = 8.56 Hz, 1H), 7.86−7.93 (m, 3H), 8.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5 (×3), 34.7, 125.8, 125.9, 126.0, 126.1 (×2), 126.5, 127.3 (×2), 127.9, 128.4, 128.6, 132.8, 134.0, 138.5, 138.7, 150.7; HRMS (EI, 70 eV) calcd for $C_{20}H_{20}$ (M^+), 260.1565, found 260.1604.

2-*p*-Tolylnaphthalene (3q) was prepared by the reaction of **1f** (35.45 mg, 0.1 mmol) with **2i** (1.0 M in Et_2O, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3q** (17.68 mg, 81%) as a white solid: mp 89−91 °C (uncorrected); TLC R_f 0.58 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.33 (d, J = 7.89 Hz, 2H), 7.49−7.54 (m, 2H), 7.71 (d, J = 8.23 Hz, 2H), 7.83 (dd, J = 1.84 Hz, 1H), 7.91−7.99 (m, 3H), 8.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 125.7, 125.8, 126.0, 126.5, 127.5 (×2), 127.9 (×2), 128.4, 128.6, 129.9 (×2), 132.8, 134.0, 137.4, 138.5, 138.8; HRMS (EI, 70 eV) calcd for $C_{17}H_{14}$ (M^+), 218.1096, found 218.1066.

1-(Dimethylamino)-5-phenylnaphthalene (3r) was prepared by the reaction of **1g** (39.75 mg, 0.1 mmol) with **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3r** (16.82 mg, 68%) as a colorless oil which was rapidly changed to be a brown oil in air: TLC R_f 0.60 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 6H), 7.09 (d, J = 7.56 Hz, 1H), 7.29−7.57 (m, 9H), 8.30 (d, J = 8.40 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.5 (×2), 114.3, 121.5, 124.0, 124.9, 126.0, 127.2, 127.4, 128.4 (×2), 129.5, 130.4 (×2), 133.3, 141.0, 141.6, 151.1; HRMS (EI, 70 eV) calcd for $C_{18}H_{17}N$ (M^+), 247.1361, found 247.1358.

1-(Dimethylamino)-5-(4-*tert*-butylphenyl)naphthalene (3s) was prepared by the reaction of **1g** (39.75 mg, 0.1 mmol) with **2b** (2.0 M in Et_2O, 0.15 mL, 0.3 mmol + 0.1 mL, 0.2 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3s** (23.21 mg, 76.5%) as a colorless oil which was rapidly changed to be a brown oil in air: TLC R_f 0.60 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.92 (s, 6H), 7.09 (d, J = 7.38 Hz, 1H), 7.32 (dd, J = 7.48, 8.48 Hz, 1H), 7.39−7.44 (m, 3H), 7.47−7.54 (m, 3H), 7.62 (d, J = 8.56 Hz, 1H), 8.28 (d, J = 8.56 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.6 (×3), 34.7, 45.5 (×2), 114.2, 121.5, 123.8, 124.9, 125.3 (×2), 125.9, 127.1, 129.5, 130.0 (×2), 133.4, 138.6, 140.9, 150.2, 151.3; HRMS (EI, 70 eV) calcd for $C_{22}H_{25}N$ (M^+), 303.1987, found 303.1974.

1-(Dimethylamino)-5-*p*-tolylnaphthalene (3t) was prepared by the reaction of **1g** (39.75 mg, 0.1 mmol) with **2i** (1.0 M in Et_2O 0.3 mL, 0.3 mmol + 0.2 mL, 0.2 mmol) in the presence of dppfNiCl$_2$. The crude compound was purified by preparative TLC (*n*-hexane) to give **3t** (18.56 mg, 71%) as a colorless oil which was rapidly changed to be a brown oil in air: TLC R_f 0.58 (ethyl acetate:*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.92 (s, 6H), 7.10 (d, J = 7.38 Hz, 1H), 7.24−7.40 (m, 6H), 7.49−7.60 (m, 2H), 8.29 (d, J = 8.56 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 45.5 (×2), 114.2, 121.6, 123.8, 125.0, 125.9, 127.2, 129.1 (×2), 129.5, 130.3 (×2), 133.4, 137.1, 138.6, 140.9, 151.2; HRMS (EI, 70 eV) calcd for $C_{19}H_{19}N$ (M^+), 261.1517, found 261.1519.

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Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra for **1a**−**i** and **3b, e, g, i, n**−**t**. This material is available free of charge via the Internet at http://pubs.acs.org.

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