JOC The Journal of Organic Chemistry
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Nickel Catalyzed Cross-Coupling of Aryl C–O Based Electrophiles with Aryl Neopentylglycolboronates

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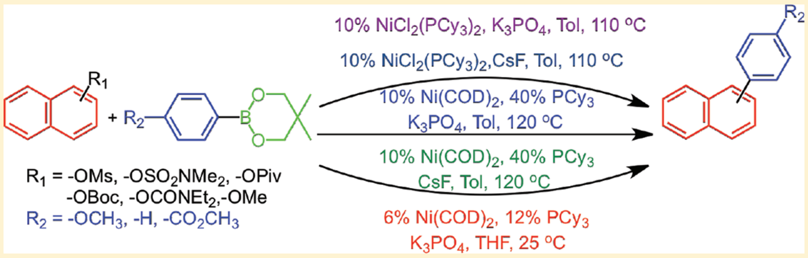
Supporting Information



ABSTRACT: The efficiency of mesylates, sulfamates, esters, carbonates, carbamates, and methyl ethers as C–O-based electrophiles attached to the 1- or 2-position of naphthalene and to activated and nonactivated phenyl substrates was compared for the first time in Ni-catalyzed cross-coupling with phenyl neopentylglycolboronates containing electron-rich and electron-deficient substituents in their *para*-position. These experiments were performed in the presence of four different Ni(II)- and Ni(0)-based catalysts. Ni(II)-based catalysts mediate the cross-coupling of most 2-naphthyl C–O electrophiles with both arylboronic acids and with neopentylglycolboronates when K_3PO_4 is used as base. The same catalysts are not efficient when CsF is used as base. However, Ni(0)-based catalysts exhibit selective efficiency, and when reactive, their efficiency is higher than that of Ni(II)-based catalysts in the presence of both K_3PO_4 and CsF. These results provide both reaction conditions for the cross-coupling, and for the elaboration of orthogonal cross-coupling methodologies of various C–O based electrophiles with aryl neopentylglycolboronates. With the exception of mesylates and sulfamates the efficiency of all other 2-naphthyl C–O electrophiles was lower in cross-coupling with aryl neopentylglycolboronates than with arylboronic acids

INTRODUCTION

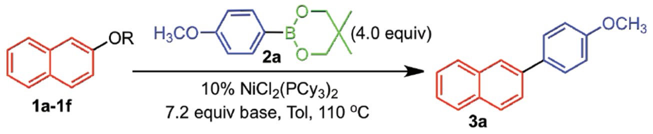
Suzuki–Miyaura cross-coupling is one of the most important reactions used in the construction of C–C bonds. Pd is widely used as the catalyst in this reaction.[1] Recently, Ni, which is less expensive and more reactive toward C–O-based electrophiles than Pd, has been employed as an alternative catalyst in Suzuki–Miyaura cross-coupling.[2] Aryl sulfonates,[3] ethers,[4] esters,[3i,5] carbonates,[6] carbamates,[6–8] sulfamates,[6,7b,8] and phosphates[9] have been elaborated as C–O-based electrophiles in cross-coupling with arylboronic acids, and for the case of aryl methyl ethers[4] also with aryl neopentylglycolboronates, all under various Ni-catalyzed conditions.

Since the first report on the Ni-catalyzed Suzuki–Miyaura cross-coupling of aryl sulfonates with arylboronic acids,[3a] interest in utilizing accessible and inexpensive C–O based electrophiles in cross-coupling continues to develop. Suzuki–Miyaura cross-coupling of aryl mesylates and tosylates with arylboronic acids using inexpensive Ni(II)-based catalysts is well established.[3d] However, in some situations, boronic esters are more favored than boronic acids in Suzuki–Miyaura cross-coupling reactions. For example, boronic esters can be used in stoichiometric amounts due to their monomeric species present under anhydrous conditions when boronic acids form anhydrides.[10] At the same time, boronic esters are less sensitive than boronic acids in some reactions such as protodeborylation.[10]

Boronic esters are prepared by the esterification of boronic acids[11] and by transition-metal-catalyzed borylation of aryl halides.[2,11] Transition-metal-catalyzed borylation provides an one-step synthesis of boronic esters.[2] Our group is interested in the development of inexpensive Ni-catalyzed borylation reactions of aryl halides[3g,12] and sulfonates[13] and of their subsequent cross-coupling. Aryl neopentylglycolboronates are less expensive and more atom economic than the currently more commonly used pinacolboronates.[12a] The versatile Ni(II)-catalyzed borylation of aryl halides and sulfonates with neopentylglycolborane generated in situ from neopentylglycol and $BH_3 \cdot S(CH_3)_2$ tolerates a variety of *ortho*-, *meta*- and *para*-electrophilic functional groups and provides excellent yields.[14,15] Some preliminary data suggested that Ni-catalysts can cross-couple aryl halides with aryl neopentylglycolboronates in moderate to good yields.[12a] Encouraged by these results, preliminary cross-coupling reactions between aryl neopentylglycolboronates and aryl sulfonates were also reported.[3g] A more comprehensive study on the cross-coupling

Received: November 7, 2011
Published: December 28, 2011

Table 1. Cross-Coupling of 2-Naphthyl-Containing C−O Electrophiles with *p*-Methoxyphenyl Neopentylglycolboronate Catalyzed by $NiCl_2(PCy_3)_2$/ K_3PO_4 or CsF in Toluene at 110 °C



entry	OR	base	time (h)	yield[a] (%)
1	OMs	K_3PO_4	12	25
2	OSO_2NMe_2	K_3PO_4	12	54
3	OPiv	K_3PO_4	12	6
4	OBoc	K_3PO_4	24	0
5	$OCONEt_2$	K_3PO_4	24	34
6	OMe	K_3PO_4	24	13
7	OMs	CsF	12	7
8	OSO_2NMe_2	CsF	12	1
9	OPiv	CsF	12	0
10	OBoc	CsF	24	0
11	$OCONEt_2$	CsF	24	0
12	OMe	CsF	24	0

[a] Isolated yield.

of aryl sulfonates and sulfamates was recently reported.[16] So far, only aryl sulfonates,[3g] sulfamates,[16] and methyl ethers[4] have been shown to be active in the cross-coupling reaction with aryl neopentylglycolboronates. However, other electrophiles such as aryl pivalates, carbonates, and carbamates have not been investigated in cross-coupling with aryl neopentylglycolboronates.

After a survey of the literature on C−O-based electrophiles in cross-coupling reactions, we found that the reaction conditions employed Ni(II)- or Ni(0)-based catalysts, ligands, boron sources, bases, solvents, and temperatures differed from one group of C−O electrophiles to another. The only comparative study on the efficiency of different C−O electrophiles was recently reported for cross-coupling with potassium aryl and heteroaryl trifluoroborates.[3i]

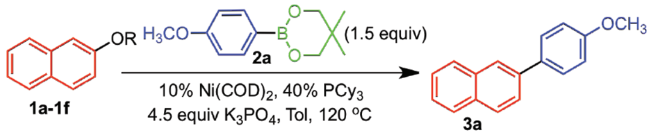
In this paper, we report the first comparative analysis of the efficiency of six different aryl-containing C−O-based electrophiles in Ni-catalyzed Suzuki−Miyaura cross-coupling with aryl neopentylglycolboronates. These experiments were performed with four different catalytic systems that were developed specifically for the cross-coupling of aryl methyl ethers[4] with aryl neopentylglycolboronates, aryl mesylates[16] with aryl neopentylglycolboronates, and respectively of aryl esters, carbamates, and carbonates with arylboronic acids[5a,6] and arylboroxines.[5b−d]

■ RESULTS AND DISCUSSION

Selection of the Ni-Based Catalysts. Nickel catalysis was used for the cross-coupling of aryl-containing C−O-based electrophiles with arylboronic acids, anhydrides, and boronic esters.[2] Different reaction conditions and catalysts are required for the cross-coupling of aryl-containing C−O-based electrophiles with arylboronic acids, anhydrides, and boronic esters. From the entire group of C−O-based electrophiles only aryl mesylates and tosylates were investigated in cross-coupling with both boronic acids and boronic esters.[2] Cross-coupling of aryl sulfonates with boronic acids proceeds in the presence of Ni(II)-based catalysts at high temperature and in the presence of Ni(0)-based catalysts at low temperature. The Ni(II)-based catalysts of choice for this reaction are $NiCl_2(PCy_3)_2/K_3PO_4$/dioxane at 130 °C[3c] and $NiCl_2$(dppe) or $NiCl_2$(dppp) both in toluene and in dioxane at temperatures between 80 and 100 °C.[3d,k] $Ni(COD)_2/PCy_3/K_3PO_4$/THF was shown to cross-couple aryl sulfonates with arylboronic acids at room temperature.[3e] Preliminary results on the cross-coupling of aryl neopentylglycolboronates demonstrated that they can cross-couple with aryl chlorides, bromides, and iodides with $NiCl_2$(dppe)/dppe/K_3PO_4 or NaOH in dioxane at 110 °C.[12a] However, the same catalyst is completely inactive in the cross-coupling of aryl neopentylglycolboronates with aryl sulfonates.[12a] Nevertheless, preliminary results demonstrated that $Ni(COD)_2/PCy_3/K_3PO_4$ in THF at room temperature is an excellent catalyst for the cross-coupling of aryl mesylates and tosylates with aryl neopentylglycolboronates.[3g] The only other C−O-based electrophile that was cross-coupled with aryl neopentylglycolboronates is the aryl methyl ether.[4] The catalyst of choice for this cross-coupling is $Ni(COD)_2/PCy_3$/CsF in toluene at 120 °C. All other C−O-based electrophiles, including esters, carbonates, carbamates, and sulfamates, were cross-coupled only with arylboronic acids by using $NiCl_2(PCy_3)_2/K_3PO_4$ in toluene, dioxane, or xylene at temperatures ranging from 80 to 150 °C.[5−8] This work was recently reviewed.[2] This manuscript reports the first comparison of the efficiency of six aryl C−O-based electrophiles in cross-coupling with aryl neopentylglycolboronates. Reaction conditions specific for individual classes of C−O electrophiles namely for aryl mesylates ($Ni(COD)_2/PCy_3/K_3PO_4$/THF/25 °C), aryl methyl ethers ($Ni(COD)_2/PCy_3$/CsF/toluene/120 °C), aryl esters, carbonates, carbamates, and sulfamates ($NiCl_2(PCy_3)_2/K_3PO_4$/toluene/110 °C), and a modified catalyst specific for aryl methyl ethers were investigated.

Efficiency of Aryl C−O-Based Electrophiles in Cross-Coupling with Aryl Neopentylglycolboronates Catalyzed by $NiCl_2(PCy_3)_2/K_3PO_4$ in Toluene at 110 °C. The reaction conditions employed by Garg's laboratory[5a,6,8] for the cross-coupling of a diversity of aryl C−O-based electrophiles including aryl-OPiv, $-OCO_2NEt_2$, -OBoc, and $-OSO_2NMe_2$ with arylboronic acids, were used to investigate the cross-coupling of all aryl C−O electrophiles with aryl neopentylglycolboronates. These conditions employ $NiCl_2(PCy_3)_2$

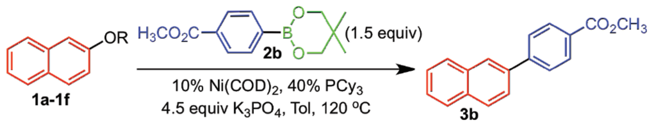
Table 2. Cross-Coupling of 2-Naphthyl-Containing C−O Electrophiles with *p*-Methoxyphenyl Neopentylglycolboronate Catalyzed by Ni(COD)$_2$/PCy$_3$/K$_3$PO$_4$ in Toluene at 120 °C



entry	OR	time (h)	yield[a] (%)
1	OMs	18	59
2	OSO$_2$NMe$_2$	18	44
3	OPiv	36	33
4	OBoc	36	17
5	OCONEt$_2$	36	23
6	OMe	36	17

[a] Isolated yield.

Table 3. Cross-Coupling of 2-Naphthyl-Containing C−O Electrophiles with *p*-Methyl Carboxylate Phenyl Neopentylglycolboronate Catalyzed by Ni(COD)$_2$/PCy$_3$/K$_3$PO$_4$ in Toluene at 120 °C



entry	OR	time (h)	yield[a] (%)
1	OMs	18	52
2	OSO$_2$NMe$_2$	18	49
3	OPiv	36	45
4	OBoc	36	24
5	OCONEt$_2$	12	40
6	OMe	36	22

[a] Isolated yield.

as catalyst and flame-dried K$_3$PO$_4$ as base in toluene at 110 °C. The results from Table 1 showed that under these conditions aryl-OMs, -OSO$_2$NMe$_2$, and -OCO$_2$NEt$_2$ gave cross-coupling products in moderate yields (25%, 54% and 34%, Table 1, entries 1, 2, and 5). However, no reaction was observed for aryl-OBoc, and only low yields were obtained for -OPiv and -OMe (6% and 13%, respectively, Table 1, entries 3 and 6). Table 1 reports also the same cross-coupling experiments in which the K$_3$PO$_4$ base was replaced with CsF. With the exception of the experiments from entries 7 and 8, which showed very low efficiency, all other experiments demonstrated that CsF is not an active base for cross-couplings performed under the reaction conditions reported in Table 1.

The yields of the biaryl products using aryl neopentylboronates were generally lower than those obtained for the cross-coupling of the same C−O electrophiles with arylboronic acids.[6,17] It was reported that a certain amount of water facilitated the transmetalation step of the cross-coupling reaction with arylboronic acids.[7a,8] However, in contrast to the reaction with arylboronic acid, no water is generated during the cross-coupling of aryl neopentylglycolboronates. Therefore, the Ni-catalysis conditions previously employed for arylboronic acids might not be the most suitable for aryl boronates.

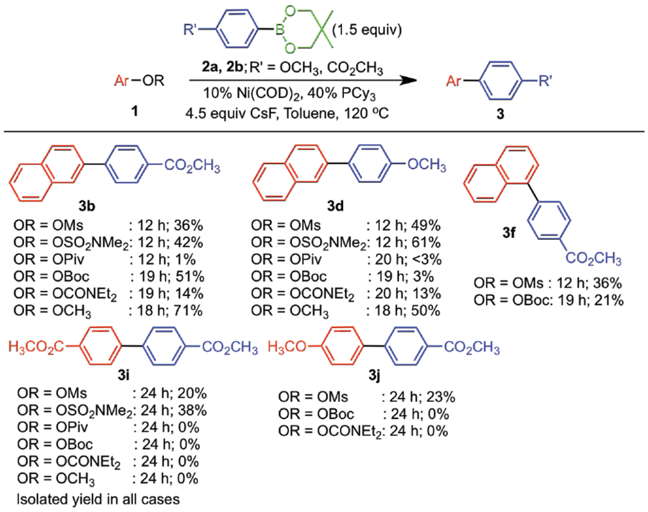
The Efficiency of Aryl C−O-Based Electrophiles in Cross-Coupling with Aryl Neopentylglycolboronates Catalyzed by Ni(COD)$_2$/K$_3$PO$_4$ in Toluene at 120 °C. The catalytic system employed by the Chatani laboratory for the cross-coupling of aryl methyl ethers with aryl neopentylglycolboronates[4] involving Ni(COD)$_2$/PCy$_3$/CsF/toluene/120 °C was modified by changing its base from CsF to K$_3$PO$_4$, dried under vacuum at 40 °C overnight, while maintaining toluene as solvent at 120 °C. All aryl C−O-based electrophiles from Table 2 were cross-coupled to a certain extent under these conditions in low to moderate yield.

However, the aryl -OBoc, which was previously inert under the NiCl$_2$(PCy$_3$)$_2$ catalysis (Table 1, entry 4), reacted under these conditions (Table 2, entry 4).

In order to explore the electronic effect of the aryl neopentylglycolboronates on the efficiency of cross-coupling, both electron-rich (Table 2) and electron-deficient (Table 3) aryl neopentylglycolboronates were studied. Under identical conditions, the electron-deficient arylboronic ester gave higher yields than the electron-rich arylboronic ester with all types of C−O-based electrophiles. Significant improvement was observed for −OCONEt$_2$ (40%) compared to 23% in the reaction with electron-rich aryl neopentylglycolboronates. The trend of the efficiency of aryl C−O-based electrophiles was found to be: -OMs (52%) > -OSO$_2$NMe$_2$ (49%) > -OPiv (45%) > -OBoc (24%) > -OMe (22%) (Table 3). A similar trend was also found for Ni-catalyzed cross-coupling of C−O based electrophiles with potassium aryl and heteroaryl trifluoroborates.[3i]

The Efficiency of Aryl C−O-Based Electrophiles in Cross-Coupling with Aryl Neopentylglycolboronates Catalyzed by Ni(COD)$_2$/PCy$_3$/CsF in Toluene at 120 °C. By using CsF as base at 120 °C, the C−O bond of aryl methyl ethers was successfully cross-coupled with aryl neopentylglycolboronates in moderate to good yields with Ni(COD)$_2$/PCy$_3$ in toluene.[4] Inspired by this work, we applied these unmodified reaction conditions to all C−O-based electrophiles. The optimized conditions for the methoxy leaving group were found to be very specific and not applicable to other leaving groups. Aryl mesylates and sulfamates were cross-coupled with moderate yields (36% to 61%) (Table 4, **3b** and **3d**; OR = OMs, OSO_2NMe_2). These results are in agreement with the results obtained when $NiCl_2(PCy_3)_2/K_3PO_4$ was used in toluene at 110 °C (Table 1, entries 1 and 2) and also $Ni(COD)_2/PCy_3/K_3PO_4$ in toluene at 120 °C (Table 2, entries 1 and 2). In addition, cross-coupling of aryl carbamates gave poor yields (13−14%, Table 4, **3b** and **3d**; OR = $OCONEt_2$) while -OPiv was almost inert (<3%) (Table 4, **3b** and **3d**; OR = OPiv). This low efficiency of the aryl ester leaving group (-OPiv) was also reported by Chatani's laboratory in cross-coupling using the same catalytic system employed for −OAc leaving group.[4] Furthermore, the efficiency of cross-coupling of -OBoc was found to be highly dependent on the electronic character of the aryl neopentylglycolboronates. With electron-deficient aryl neopentylglycolboronates, a moderate yield (51%) was isolated (Table 4, **3b**; OR = OBoc). However, with electron-rich aryl neopentylglycolboronates, almost no product was separated (3%) (Table 4, **3d**; OR = OBoc). Cross-coupling of *ortho*-substituted aryl carbonate substrate gave a diminished yield (21%) (Table 4, **3f**; OR = OBoc). Aryl methyl ether substrates cross-coupled with aryl neopentylglycolboronate with the highest yields compared to other C−O electrophiles (50% and 71%) (Table 4, **3b** and **3d**; OR = OMe). These results contrast with reactions carried out with the same Ni-catalyst but K_3PO_4 as base (Table 2, entry 6 and Table 3, entry 6). Thus, by changing the base from K_3PO_4 to CsF, the efficiency of electrophiles was completely different. This observation may have significant implications for synthetic applications such as the orthogonal cross-coupling of aryl derivatives containing the methoxy group as an electrophile and the less reactive electrophiles -OPiv, -OBoc, and $-OCONEt_2$ as inert functional groups. Phenol derivatives generally were less reactive than naphthol derivatives due to the higher activation energy of C−O bond in the oxidative addition step.[4] Only substituted phenyl mesylates and sulfamates were coupled with poor yield (Table 4, **3i** and **3j**; OR = OMs, OSO_2NMe_2).

Table 4. Cross-Coupling of Aryl Containing C−O Electrophiles with *Para*-Substituted Aryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3$/CsF in Toluene at 120 °C



3b
OR = OMs : 12 h; 36%
OR = OSO_2NMe_2: 12 h; 42%
OR = OPiv : 12 h; 1%
OR = OBoc : 19 h; 51%
OR = $OCONEt_2$: 19 h; 14%
OR = OCH_3 : 18 h; 71%

3d
OR = OMs : 12 h; 49%
OR = OSO_2NMe_2: 12 h; 61%
OR = OPiv : 20 h; <3%
OR = OBoc : 19 h; 3%
OR = $OCONEt_2$: 20 h; 13%
OR = OCH_3 : 18 h; 50%

3f
OR = OMs : 12 h; 36%
OR = OBoc: 19 h; 21%

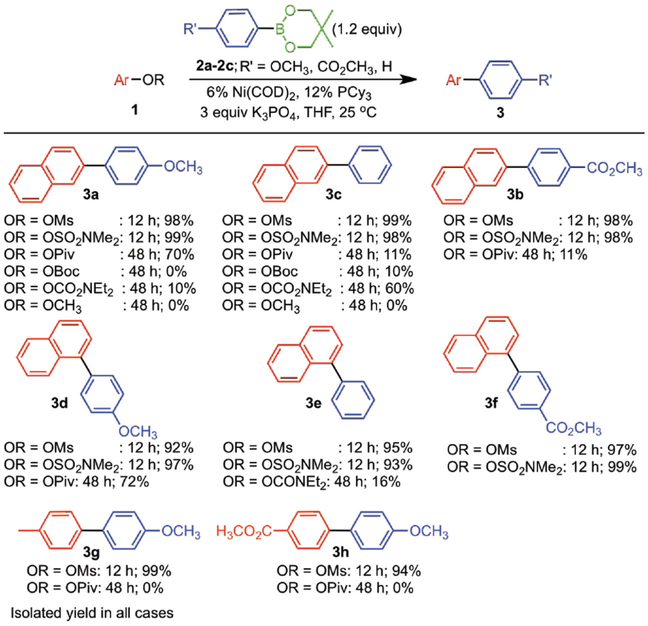
3i
OR = OMs : 24 h; 20%
OR = OSO_2NMe_2: 24 h; 38%
OR = OPiv : 24 h; 0%
OR = OBoc : 24 h; 0%
OR = $OCONEt_2$: 24 h; 0%
OR = OCH_3 : 24 h; 0%

3j
OR = OMs : 24 h; 23%
OR = OBoc : 24 h; 0%
OR = $OCONEt_2$: 24 h; 0%

Isolated yield in all cases

The Efficiency of Aryl C−O-Based Electrophiles in Cross-Coupling with Aryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3/K_3PO_4$ in THF at 25 °C. First introduced by Hu laboratory[3e] for cross-coupling of aryl tosylates with arylboronic acids, the catalytic system $Ni(COD)_2/PCy_3/K_3PO_4$ in THF has been subsequently employed for the cross-coupling of aryl mesylates and sulfamates with aryl neopentylglycolboronates.[3g,16] This catalytic system is very efficient for the cross-coupling of aryl sulfonates and sulfamates at room temperature regardless of the electronic properties and steric hindrances of both substrates.[16] Therefore, we applied these reaction conditions to all six aryl C−O-based electrophiles. Among the C−O-based eletrophiles investigated, mesylates and sulfamates were cross-coupled with excellent yields (92−99%) (Table 5, **3a−f**; OR = OMs, OSO_2NMe_2). The efficiency of naphthyl pivalates is determined by the electronic properties of the aryl neopentylglycolboronate used in the reaction. The -OPiv was more reactive toward eletron-rich aryl neopentylglycolboronates (70% and 72%) (Table 5, **3a** and **3d**; OR = OPiv) than electron-deficient derivatives (11%) (Table 5, **3b**; OR = OPiv).

Table 5. Cross-Coupling of Aryl-Containing C−O Electrophiles with *Para*-Substituted Aryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3/K_3PO_4$ in THF at 25 °C



3a
OR = OMs : 12 h; 98%
OR = OSO_2NMe_2: 12 h; 99%
OR = OPiv : 48 h; 70%
OR = OBoc : 48 h; 0%
OR = OCO_2NEt_2 : 48 h; 10%
OR = OCH_3 : 48 h; 0%

3c
OR = OMs : 12 h; 99%
OR = OSO_2NMe_2: 12 h; 98%
OR = OPiv : 48 h; 11%
OR = OBoc : 48 h; 10%
OR = OCO_2NEt_2 : 48 h; 60%
OR = OCH_3 : 48 h; 0%

3b
OR = OMs : 12 h; 98%
OR = OSO_2NMe_2: 12 h; 98%
OR = OPiv: 48 h; 11%

3d
OR = OMs : 12 h; 92%
OR = OSO_2NMe_2: 12 h; 97%
OR = OPiv: 48 h; 72%

3e
OR = OMs : 12 h; 95%
OR = OSO_2NMe_2: 12 h; 93%
OR = $OCONEt_2$: 48 h; 16%

3f
OR = OMs : 12 h; 97%
OR = OSO_2NMe_2: 12 h; 99%

3g
OR = OMs: 12 h; 99%
OR = OPiv: 48 h; 0%

3h
OR = OMs: 12 h; 94%
OR = OPiv: 48 h; 0%

Isolated yield in all cases

No reaction was observed for substituted phenyl pivalates (Table 5, **3g** and **3h**; OR = OPiv). At room temperature, aryl methyl ethers remained unreactive while carbonates gave diminished yields (<10%) (Table 5, **3a**, **3c**; OR = OBoc).

Comparison of the Efficiency of Different Electrophiles in Cross-Coupling Reactions with 4-Methoxy Phenyl Neopentylglycolboronates. As observed from previous series of experiments (Tables 1−5) and by their summary from Figure 1 (conditions 0−5), aryl mesylates and sulfamates are more efficient than the other C−O-based electrophiles regardless of the catalyst used. $Ni(COD)_2/PCy_3/K_3PO_4$ in THF at room temperature provides the best conditions for the cross-coupling of aryl mesylates, sulfamates, and pivalates with aryl neopentylglycolboronates. This catalyst

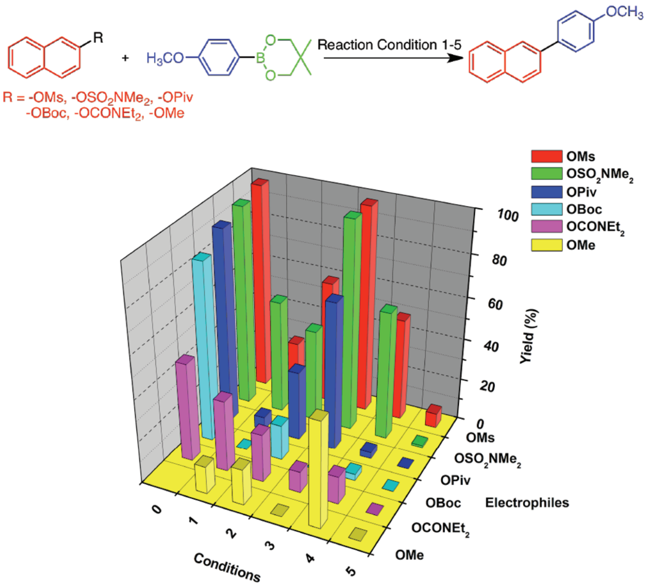


Figure 1. Comparison of the efficiency of 2-naphthyl C−O electrophiles in the cross-coupling reaction with 4-methoxyphenylboronic acid (0) and 4-methoxyphenyl neopentylglycolboronate (0−5): (0) 5%(pivalate), 10% (for the rest) NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene/130 °C[5a,6] except for OMs where 1% NiCl$_2$(dppp)/K$_3$PO$_4$/dioxane/100 °C was used;[3k] (1) 10% NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene/110 °C; (2) 10% Ni(COD)$_2$/40% PCy$_3$/K$_3$PO$_4$/toluene/120 °C; (3) 6% Ni(COD)$_2$/12% PCy$_3$/K$_3$PO$_4$/ THF/25 °C; (4) 10% Ni(COD)$_2$/40% PCy$_3$/CsF/toluene/120 °C; (5) 10% NiCl$_2$(PCy$_3$)$_2$/CsF/toluene/110 °C.

is not efficient for carbonates and methyl ethers and exhibits poor efficiency for carbamates.

By contrast, Ni(COD)$_2$/PCy$_3$/CsF in toluene at 120 °C is the best catalyst for the cross-coupling of aryl methyl ethers, although this catalyst is also active for aryl mesylates and sulfamates (Figure 1). This catalytic system is not efficient toward aryl pivalates and carbonates but shows low efficiency toward aryl carbamates. Ni(COD)$_2$/PCy$_3$/K$_3$PO$_4$/toluene at 120 °C as a catalytic system was found to be active but less efficient and at the same time less selective for all substrates. NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene at 110 °C is the least efficient of all catalysts but exhibits selectivity that is complementary to Ni(COD)$_2$-based catalytic systems. The replacement of K$_3$PO$_4$ base from this catalyst with CsF decreases its efficiency even more. Column (0) of Figure 1 compares also literature data for the cross-coupling of the same C−O electrophiles in cross-coupling with 4-methoxyphenylboronic acid with NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene at 130 °C.[5a,6] This is the catalyst of choice employed in Garg laboratory[5,6,8] for the cross-coupling of aryl C−O electrophiles with arylboronic acids. Only the cross-coupling of 2-naphthyl mesylate with 4-methoxyphenylboronic acid was selected from experiments catalyzed with NiCl$_2$(dppp)/K$_3$PO$_4$/dioxane/100 °C.[3k] These results are self-explanatory. Arylboronic acids are more efficient than aryl neopentylglycolboronates when NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$ in toluene at high temperature is used (compare columns 0 and 1 in Figure 1). When the K$_3$PO$_4$ base was replaced with CsF the catalyst became inefficient for the cross-coupling of all C−O electrophiles with aryl neopentylglycolbononates. Nevertheless, the efficiency of the cross-coupling of 2-naphthyl mesylates and sulfamates with aryl neopentylglycolboronate catalyzed with Ni(COD)$_2$/ PCy$_3$/K$_3$PO$_4$/THF at 25 °C is comparable with that of the same electrophiles cross-coupled with arylboronic acids when catalyzed with NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene at 130 °C (Figure 1). This result is remarkable. The electronic properties of aryl neopentylglycolboronates also influence on the efficiency of C−O electrophiles. Electron-deficient aryl boronates gave higher yields than electron-rich aryl boronates under the same conditions.

■ CONCLUSIONS

The efficiency of aryl mesylates, sulfamates, pivalates, carbonates, carbamates, and methyl ethers was investigated for the first time in Ni-catalyzed cross-coupling with aryl neopentylglycolboronates. Five different catalytic systems and reaction conditions that are specific for aryl mesylates with aryl neopentylglycolboronates, aryl methyl ethers with aryl neopentylglycolboronates, aryl sulfamates, pivalates, carbonates, and carbamates with arylboronic acids were applied to all six aryl C−O-based electrophiles. A catalytic system based on modified conditions for aryl methyl ethers was also investigated. It was shown that the optimum catalyst for aryl mesylates, Ni(COD)$_2$/PCy$_3$/K$_3$PO$_4$/THF/25 °C, is the most efficient not only for mesylates but also for aryl sulfamates and pivalates and the least efficient for carbonates, carbamates and methyl ethers. Therefore, this catalytic system is very selective and may be able to provide for the first time orthogonal reaction conditions for the cross-coupling of aryl mesylates, sulfamates, and pivalates in the presence of aryl carbonates, carbamates and methyl ethers in cross-coupling with aryl neopentylglycolboronates. Previously, orthogonal conditions were reported only for the cross-coupling of arylboronic acids with aryl sulfamates in the presence of aryl carbamates and aryl methyl ethers.[8] The reaction conditions Ni(COD)$_2$/PCy$_3$/CsF/toluene/120 °C are the most efficient for the cross-coupling of aryl methyl ethers and provide moderate yields for aryl mesylates and sulfamates while displaying little efficiency for aryl pivalates, carbonates, and carbamates. Therefore, these are orthogonal reaction conditions for the cross-coupling of aryl methyl ethers, mesylates and sulfamates with aryl neopentylglycolboronates in the presence of aryl pivalates, carbonates and carbamates. The catalytic system Ni(COD)$_2$/PCy$_3$/K$_3$PO$_4$/toluene/120 °C and the same catalyst in the presence of CsF are the least selective, generating comparable yields with all C−O electrophiles. NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene/110 °C is most efficient for sulfamates, carbamates, and mesylates in all cases with moderate yields and is inefficient for pivalates, carbonates, and methyl ethers. Therefore, this catalyst provides also chemical orthogonality although with much lower efficiency. The efficiency of 2-naphthyl-containing C−O electrophiles was also compared with literature data for cross-coupling with NiCl$_2$(PCy$_3$)$_2$/K$_3$PO$_4$/toluene/130 °C. This comparison showed that with the exception of aryl mesylates and sulfamates cross-coupled with aryl neopentylglycolboronates in the presence of Ni(COD)$_2$/PCy$_3$/K$_3$PO$_4$/THF/25 °C, aryl containing C−O electrophiles are more efficient in cross-coupling with arylboronic acids than with the corresponding aryl neopentylglycolboronates. At the same time, catalytic systems based on Ni(II) are nonselective toward C−O electrophiles regardless of whether they are cross-coupled with arylboronic acids or with aryl neopentylglycolboronates, while all catalytic systems based on Ni(0) exhibit high selectivity for the cross-coupling of aryl C−O-based electrophiles with aryl neopentylglycolboronates. The selectivity of Ni(0)-based catalysts for aryl neopentylglycolboronates toward C−O based electrophiles contrasts the lack of selectivity observed for the same electrophiles in cross-coupling with potassium aryltrifluoroborates.[3i]

EXPERIMENTAL SECTION

General Experimental Methods. 1-Naphthol, 2-naphthol, *p*-cresol, methyl 4-hydroxybenzoate, *N*,*N*-dimethylsulfamoyl chloride, methanesulfonyl chloride, pivaloyl chloride, di-*tert*-butyl dicarbonate, *N*,*N*-diethylcarbamoyl chloride, iodomethane, DMAP, NaH, Ni(COD)$_2$ (98+%), PCy$_3$, and CsF were used as received from commercial sources. Toluene, triethylamine, pyridine, DMF, DME, and dichloromethane were distilled over CaH_2 and stored under nitrogen prior to use. THF from commercial source was distilled over sodium and benzophenone and stored under nitrogen prior to use. K_3PO_4 from a commercial source was dried at 40 °C under vacuum overnight and kept in a desiccator prior to use or flame dried as specified in Results and Discussion section. $NiCl_2(PCy_3)_2$, naphthalen-1-yl pivalate, (**1i**), *p*-tolyl pivalate (**1v**), and naphthalen-2-yl pivalate (**1c**) were synthesized according to literature procedure.[5a] 2-Methanesulfonyloxynaphthalene (**1a**) 4-methoxyphenyl methanesulfonate (**1r**), *p*-tolyl methanesulfonate (**1u**), and methyl 4-((methylsulfonyl)oxy)benzoate (**1l**) were prepared according to literature method.[13] Naphthalen-1-yl dimethylsulfamate (**1h**), *tert*-butyl naphthalen-1-yl carbonate (**1j**), *tert*-butyl naphthalen-2-yl carbonate (**1d**), naphthalen-1-yl diethylcarbamate (**1k**), and naphthalen-2-yl diethylcarbamate (**1e**) were synthesized according to the literature procedure.[6] Methyl 4-methoxybenzoate (**1q**)[18] and 4-methoxyphenyl dimethylsulfamate (**1m**)[16] were prepared by following the literature procedures. 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**2a**), methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (**2b**), and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2c**) were prepared according to the literature procedures.[12b,14,15] ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using TMS as internal standard. High-resolution mass spectra of new compounds were obtained on a high-resolution double focusing chemical ionization mass spectrometer. A GC coupled with an FID detector and column HP 19091J-413 (5%-phenyl)-methylpolysiloxane 30 m length 0.32 mm internal diameter was used to follow the reaction conversions and to assess purity of final compounds complementary to the NMR technique. The crude reaction mixtures were diluted with THF and analyzed by GC as reported in previous related publications from our laboratory.[13−16]

Typical Procedure for the Synthesis of Aryl Sulfamates. The aryl sulfamates were prepared according to a literature procedure.[6]

*Naphthalen-2-yl Dimethylsulfamate(**1b**).* To an oven-dried round-bottom flask equipped with a stirring bar was added under nitrogen atmosphere NaH (25.0 mmol, 0.58 g). The flask was cooled to 0 °C, and 2-naphthol (20.8 mmol, 3.0 g) in dried DME (25 mL) was added dropwise at 0 °C. The reaction mixture was allowed to stir at room temperature for 10 min and then was cooled to 0 °C. Dimethyl sulfamoyl chloride (25.0 mmol, 3.74 g) in DME (4 mL) was added dropwise and the reaction was allowed to stir at room temperature for 12 h. The reaction was quenched by addition of water followed by the evaporation of the solvent. The solid was dissolved by Et_2O and washed with 1 M KOH and water. The combined aqueous layers were extracted with Et_2O, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography with dichloromethane/hexane (3/7) as eluent to give a white solid (4.49 g, 86%): mp =74−75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92−7.82 (m, 3H), 7.77 (d, *J* = 2.3, 1H), 7.52 (m, 2H), 7.43 (dd, *J* = 8.9, 2.4, 1H), 3.03 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 133.8, 131.9, 130.1, 127.93, 127.91, 127.0, 126.3, 120.9, 119.1, 38.9; HRMS (CI+) calcd for $C_{12}H_{13}NNaO_3S$ (M^+ + Na) 274.0514, found 274.0526.

Typical Procedure for the Synthesis of Aryl Ethers. *2-Methoxynaphthalene(**1f**).* To an oven-dried round-bottom flask equipped with a stirring bar was added under nitrogen atmosphere NaH (30.0 mmol, 0.72 g). The flask was cooled to 0 °C, and anhydrous DMF (25 mL) was added. 2-Naphthol (30.0 mmol, 4.32 g) was added slowly during stirring at 0 °C. The resulting clear solution was stirred during the rapid addition of iodomethane (37.0 mmol, 5.25 g). The reaction mixture was allowed to stir at room temperature for 3 h. The reaction was quenched with water and extracted with EtOAc. The combined organic phase was washed with 10% NaOH, water, and brine, then dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography with CH_2Cl_2 as an eluent to give a white solid (4.0 g, 84%): mp =73−75 °C (lit.[19] mp 73−74 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.70 (m, 3H), 7.43 (t, *J* = 7.5, 1H), 7.33 (dd, *J* = 11.0, 3.9, 1H), 7.19−7.11 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 134.7, 129.5, 129.1, 127.8, 126.9, 126.5, 123.7, 118.9, 105.9, 55.4.

Typical Procedure for the Synthesis of Aryl Mesylates. The aryl mesylates were prepared according to a literature procedure.[13]

*1-Methanesulfonyloxynaphthalene (**1g**).*[3h] To an oven-dried round-bottom flask equipped with a stirring bar was added under nitrogen atmosphere 1-naphthol (20 mmol, 2.88 g) and freshly distilled dichloromethane (20 mL) followed by anhydrous pyridine (8.0 mL). The reaction mixture was cooled to 0 °C before methanesulfonyl chloride (24.0 mmol, 2.80 g) was added dropwise. The reaction was allowed to stir at 0 °C for 4 h at room temperature until TLC demonstrated the consumption of the starting material. The reaction was quenched by addition of water. The aqueous phase was extracted with CH_2Cl_2 three times, and all of the combined organic layers were washed with 15% HCl and brine and dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography to give a pale yellow oil (3.98 g, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3, 1H), 7.90 (d, *J* = 7.5, 1H), 7.82 (d, *J* = 8.1, 1H), 7.64−7.52 (m, 3H), 7.48 (t, *J* = 7.9, 1H), 3.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 134.1, 127.2, 126.5, 126.4, 126.14, 126.13, 124.5, 120.6, 117.54, 37.1.

Typical Procedure for the Synthesis of Aryl Pivalates. The aryl pivalates were prepared according to a literature procedure.[5a]

*Methyl 4-(Pivaloyloxy)benzoate (**1n**).* Dry triethylamine (36.1 mmol, 5 mL) and DMAP (3.0 mmol, 0.39 g) were added at room temperature into a solution of methyl 4-hydroxybenzoate (30.0 mmol, 4.56 g) and dry CH_2Cl_2 (25 mL). Pivaloyl chloride (36.2 mmol, 4.5 mL) was added slowly during stirring, and the reaction mixture was allowed to stir at room temperature for 12 h. The organic phase was washed with saturated ammonium chloride solution and brine. The aqueous phase was extracted with EtOAc. The organic phase was combined, dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give a white solid (6.95 g, 98%), mp = 58.5−60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8, 2H), 7.14 (d, *J* = 8.8, 2H), 3.91 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 166.5, 155.0, 131.3, 121.7, 90.6, 52.3, 39.4, 27.2; HRMS (CI+) calcd for $C_{13}H_{17}O_4$ (M^+ + H) 237.1127, found 237.1118.

Typical Procedure for the Synthesis of Aryl Carbonates. The aryl carbonates were prepared according to a literature procedure.[6]

Methyl 4-((tert-Butoxycarbonyl)oxy)benzoate[20] *(**1o**).* To an oven-dried round-bottom flask equipped with stirring bar under nitrogen were added methyl 4-hydroxybenzoate (8.0 mmol, 1.22 g), dimethylaminopyridine (0.80 mmol, 0.98 g), and freshly distilled CH_2Cl_2 (20 mL). Triethylamine (8.8 mmol, 0.89 g) and di-*tert*-butyl dicarbonate (8.8 mmol, 1.87 g) were added at room temperature. The reaction mixture was allowed to stir until the bubbling subsided. The solution was washed with 0.5 M $NaHSO_4$, and the aqueous layer was extracted with CH_2Cl_2. The organic phase was combined, dried over $MgSO_4$, and filtered. The solution was evaporated under reduced pressure, and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give the product as a white solid (2.00 g, 99%): mp = 83−84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6, 2H), 7.25 (d, *J* = 8.7, 2H), 3.91 (s, 3H), 1.56 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 154.8, 151.2, 131.2, 127.7, 121.3, 84.2, 52.3, 27.8; HRMS (CI+) calcd for $C_{13}H_{17}O_5$ (M^++H) 253.1076, found 253.1067.

*tert-Butyl (4-Methoxyphenyl)carbonate (**1s**).* Following the typical procedure for the synthesis of aryl carbonates: white solid (90%); mp = 65−66.5 °C (lit.[21] mp 66−67 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.08 (d, J = 9.0, 2H), 6.88 (d, J = 9.1, 2H), 3.79 (s, 3H), 1.55 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 201.2, 156.4, 151.5, 143.9, 121.2, 113.5, 82.5, 54.8, 26.9.

Typical Procedure for the Synthesis of Aryl Carbamates. The aryl carbamates were prepared according to a literature procedure.[6]

*Methyl 4-((Diethylcarbamoyl)oxy)benzoate[22] (**1p**).* To an oven-dried round-bottom flask equipped with a stirring bar was added under nitrogen atmosphere NaH (15.6 mmol, 0.37 g). The flask was cooled to 0 °C, and methyl 4-hydroxybenzoate (13.0 mmol, 1.98 g) in dried DME (5 mL) was added dropwise at 0 °C. The reaction mixture was allowed to stir at room temperature for 10 min and then was cooled to 0 °C. Diethylcarbamoyl chloride (15.6 mmol, 2.12 g) in DME (5 mL) was added dropwise, and the reaction was allowed to stir at room temperature for 12 h. The reaction was quenched by addition of water followed by the evaporation of the solvent. The solid was dissolved by Et$_2$O and washed with 1 M KOH and water. The combined aqueous layers were extracted with Et$_2$O, washed with brine, and dried over MgSO$_4$. The solvent was evaporated, and the crude product was purified by column chromatography with 0−4% EtOAC/CH$_2$Cl$_2$ as eluent to give a colorless oil (0.89 g, 27%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 8.5, 2H), 7.20 (d, J = 8.6, 2H), 3.90 (s, 3H), 3.47−3.36 (m, 4H), 1.26 (t, J = 6.9, 3H), 1.21 (t, J = 6.9, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.6, 155.4, 153.5, 131.1, 127.0, 121.7, 52.2, 42.5, 42.1, 14.4, 13.4.

*4-Methoxyphenyl Diethylcarbamate[22] (**1t**).* Following the typical procedure of the synthesis of aryl carbamates. Column chromatography (SiO$_2$; 0 −20% EtOAc/CH$_2$Cl$_2$), colorless oil (73%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.03 (d, J = 9.0, 2H), 6.87 (d, J = 9.0, 2H), 3.79 (s, 3H), 3.48−3.31 (m, 4H), 1.26−1.17 (m, J = 23.5, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 155.9, 155.8, 153.8, 144.3, 121.7, 113.4, 54.8, 41.4, 41.0, 13.4, 12.5.

Preparation of Neopentylglycolborane. A procedure elaborated previously in our laboratory was used.[13−15] To a cooled solution (0 °C) of neopentylglycol (6.0 mmol, 2.0 equiv) in toluene (3 mL) was slowly added (CH$_3$)$_2$S·BH$_3$ (6.0 mmol, 2.0 equiv) under nitrogen. The reaction was allow to stir at 0 °C for 30 min and then at room temperature for 90 min. The neopentylglycolborane was used directly without further purification.

General Procedure for Neopentylglycolborylation. The arylboronic esters were prepared according to literature procedures.[13−15] To an oven-dried 25 mL Schlenk tube were added Zn powder (6.0 mmol, NiCl$_2$(dppp) (1.5 mmol), and PPh$_3$ (3.0 mmol) along with the appropriate aryl halides (if it is solid) (3.0 mmol). The aryl halide, catalyst, and PPh$_3$ were degassed by pumping and backfilling with nitrogen three times. Dry toluene (3 mL) was added to the reaction mixture along with the appropriate aryl halide (if it is liquid) and Et$_3$N (9.0 mmol). Neopentylglycolborane was added dropwise to the reaction mixture. The reaction was placed into an oil bath at 100 °C with stirring under nitrogen. After completion of the starting material, the reaction was quenched by the addition of a saturated NH$_4$Cl solution and extracted with EtOAc three times. The combined organic fractions were dried over MgSO$_4$, followed by filtration and evaporation of the solvent. The crude product was purified by column chromatography.

General Procedure for Cross-Coupling. *Method A (in Table 1).*[5a,6,8] To an oven-dried test tube (15 × 85 mm) were added the naphthyl C−O electrophile (0.3 mmol), neopentylglycol boronic ester (1.2 mmol, 4 equiv), and NiCl$_2$(PCy$_3$)$_2$ (0.03 mmol, 0.10 equiv). The tube was taken into the glovebox, and the anhydrous base (CsF, used as received and kept in the glovebox after first opened, and K$_3$PO$_4$, dried by flame drying and kept in the glovebox) (2.16 mmol, 7.2 equiv) was added. Dried toluene (1.0 mL) was then added, and the tube was capped with a rubber septum, which was wrapped with copper wire. The tube was taken outside the glovebox and stirred at 110 °C for 12 or 24 h (see Table 1). The crude mixture was filtered through a short column of silica gel and washed with THF. The solvent was evaporated, and the product was purified by column chromatography with dichloromethane/hexane.

Method B (in Tables 2 and 3). To an oven-dried test tube (15 × 85 mm) were added the naphthyl C−O electrophile (0.3 mmol), neopentylglycol boronic ester (0.45 mmol, 1.5 equiv), and K$_3$PO$_4$, dried under vacuum at 40 °C overnight (1.35 mmol, 4.5 equiv). The tube was taken into the glovebox, and PCy$_3$ (0.12 mmol, 0.40 equiv) and Ni(COD)$_2$ (0.03 mmol, 0,10 equiv) were added. Dried THF (1.0 mL) was then added, and the tube was capped with rubber septum, which was wrapped with copper wire. The tube was taken outside the glovebox and stirred at 120 °C for 12−36 h (see Tables 2 and 3). The crude mixture was filtered through a short column of silica gel and washed with THF. The solvent was evaporated, and the product was purified by column chromatography with dichloromethane/hexane.

Method C (in Table 4).[4] To an oven-dried test tube (15 × 85 mm) were added the aryl C−O electrophile (0.3 mmol) and the aryl neopentylglycol boronic ester (0.45 mmol, 1.5 equiv). The tube was taken into the glovebox, and CsF (1.35 mmol, 4.5 equiv), PCy$_3$ (0.12 mmol, 0.40 equiv), and Ni(COD)$_2$ (0.03 mmol, 0,10 equiv) were added. Dried toluene (1.0 mL) was then added, and the tube was capped with rubber septum, which was wrapped with copper wire. The tube was taken outside the glovebox and stirred at 120 °C for 12 or 24 h (see Table 4). The crude mixture was filtered through a short column of silica gel and washed with THF. The solvent was evaporated, and the product was purified by column chromatography with dichloromethane/hexane or hexane as eluent.

Method D (in Table 5).[16] To an oven-dried test tube (15 × 85 mm) were added the aryl C−O electrophile (0.3 mmol), the aryl neopentylglycol boronic ester (0.36 mmol, 1.2 equiv), and K$_3$PO$_4$, dried under vacuum at 40 °C overnight (0.9 mmol, 3 equiv). The tube was taken into the glovebox, and PCy$_3$ (0.036 mmol, 0.12 equiv) and Ni(COD)$_2$ (0.018 mmol, 0.06 equiv) were added. Dried THF (1.0 mL) was then added, and the tube was capped with a rubber septum. Inside the glovebox, the reaction was stirred at room temperature under nitrogen for 12−48 h (see Table 5). The crude mixture was filtered through a short column of silica gel and washed with THF. The solvent was evaporated and the product was purified by column chromatography with hexane, dichloromethane/hexane, or dichloromethane as eluent.

*2-(4-Methoxyphenyl)naphthalene (**3a**):* white solid; mp 130−131 °C (lit.[23] mp 131−133 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, J = 8.2, 1H), 7.72 (d, J = 8.5, 2H), 7.47−7.40 (m, 1H), 7.37−7.29 (m, 1H), 7.18−7.09 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.4, 137.3, 132.9, 132.8, 131.5, 127.6, 127.5, 127.2, 126.8, 125.4, 124.8, 124.6, 124.2, 113.5, 54.5.

*Methyl 4-(naphthalen-2-yl)benzoate[24] (**3b**):* white solid; mp 149−150 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.14 (d, J = 8.5, 2H), 8.07 (d, J = 1.3, 1H), 7.96−7.84 (m, 3H), 7.77 (d, J = 8.5, 2H), 7.74 (dd, J = 8.5, 1.8, 1H), 7.54−7.47 (m, 2H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.1, 145.6, 137.4, 133.7, 133.1, 130.3, 129.0, 128.8, 128.5, 127.8, 127.4, 126.6, 126.5, 126.5, 125.3, 52.3.

*2-Phenylnaphthalene (**3c**):* white solid; mp 98−99 °C (lit.[23] mp 100−101 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.04 (s, 1H), 7.93−7.84 (m, 3H), 7.77−7.70 (m, 3H), 7.53−7.45 (m, 4H), 7.38 (dd, J = 10.6, 4.2, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 141.3, 138.7, 133.8, 132.8, 129.0, 128.6, 128.4, 127.8, 127.6, 127.5, 126.4, 126.07, 125.95, 125.8.

*1-(4-Methoxyphenyl)naphthalene (**3d**):* white solid; mp 110−111 °C (lit.[3i] mp 112−113 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.99 (s, 1H), 7.92−7.83 (m, 3H), 7.72 (dd, J = 8.5, 1.8, 1H), 7.67 (d, J = 8.8, 2H), 7.52−7.44 (m, 2H), 7.03 (d, J = 8.8, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.1, 139.1, 133.0, 132.3, 131.0, 130.3, 127.4, 126.5, 126.1, 125.2, 125.1, 124.9, 124.6, 112.9, 54.5.

*1-Phenylnaphthalene[23] (**3e**):* colorless liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, J = 7.6, 2H), 7.83 (d, J = 8.1, 1H), 7.52−7.43 (m, 6H), 7.43−7.37 (m, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.9, 140.4, 133.9, 131.7, 130.2, 128.4, 127.8, 127.4, 127.0, 126.2, 125.9, 125.5.

*Methyl 4-(naphthalen-1-yl)benzoate (**3f**):* white solid; mp 62−63 °C (lit.[25] mp 65.5−66.5 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, J

= 8.3, 2H), 7.91 (dd, J = 13.6, 8.2, 2H), 7.84 (d, J = 8.5, 1H), 7.58 (d, J = 8.3, 2H), 7.56−7.49 (m, 2H), 7.47−7.41 (m, 2H), 3.97 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.2, 145.8, 139.3, 133.9, 131.4, 130.3, 129.7, 129.2, 128.6, 128.4, 127.1, 126.5, 126.1, 125.8, 125.5, 52.3.

4-Methoxy-4′-methyl-1,1′-biphenyl ***(3g)*:** white solid, mp 103−104 °C (lit.[26] mp 103−104 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, J = 8.8, 2H), 7.45 (d, J = 8.1, 2H), 7.23 (d, J = 7.8, 2H), 6.97 (d, J = 8.8, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.8, 137.9, 136.3, 133.7, 129.3, 127.9, 126.5, 114.1, 55.3, 21.0.

Methyl 4′-methoxy(1,1′-biphenyl)-4-carboxylate ***(3h)*:** white solid; mp 172−173 °C (lit.[12a] mp 173−174 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.07 (d, J = 8.3, 2H), 7.62 (d, J = 8.3, 2H), 7.57 (d, J = 8.7, 2H), 6.99 (d, J = 8.7, 2H), 3.93 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.0, 159.8, 145.1, 132.3, 130.0, 128.3, 128.2, 126.4, 114.3, 55.3, 52.0.

Dimethyl (1,1′-biphenyl)-4,4′-dicarboxylate ***(3i)*:** white solid; mp 212−214 °C (lit.[27] mp 215.5−216.5 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 (d, J = 8.2, 4H), 7.69 (d, J = 8.2, 4H), 3.95 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.9, 144.5, 130.3, 129.9, 127.4, 52.3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of compounds **1b**, **1f**, **1g**, **1n**−**p**, **1s**, **1t**, and **3a**−**j**. This information is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

Financial support by the NSF (DMR-1066116 and DMS-0935165) and by the P. Roy Vagelos Chair at Penn is gratefully acknowledged. P.L. is a graduate fellow of the Royal Thai Government. Dr. Rakesh Kohli (University of Pennsylvania) is acknowledged for obtaining HRMS data.

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