

Cross-Coupling Reactions

Deutsche Ausgabe: DOI: 10.1002/ange.201608724
Internationale Ausgabe: DOI: 10.1002/anie.201608724Palladium(0)-Catalyzed Intermolecular Arylative Dearomatization of β -Naphthols

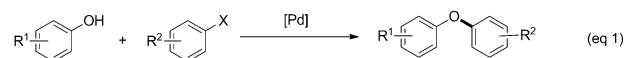
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Abstract: The first Pd^0 -catalyzed intermolecular arylative dearomatization of β -naphthols with aryl halides is described. It was found that Q-Phos could facilitate the palladium-catalyzed cross-coupling-type dearomatization of β -naphthols, while avoiding O-arylation, to construct 2-naphthalenones in excellent yields and with high chemoselectivity.

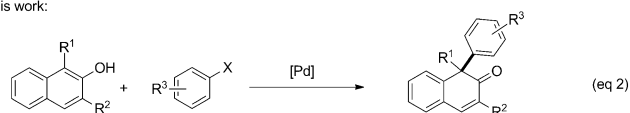
Phenol derivatives are important chemical starting materials and widely used in organic synthesis.^[1] Dearomatization of phenol derivatives provides an efficient and straightforward approach to cyclic enones, which are popular structural motifs in functional molecules.^[2,3] Palladium-catalyzed cross-coupling reactions have been applied in the dearomatization of phenol derivatives.^[4–8] However, to date, the reported works are mainly limited to intramolecular reactions, which can avoid the competitive Friedel–Crafts-type reaction, and coupling reaction with phenol oxygen nucleophile, by efficiently forming favorable five or six-membered rings. However, the intramolecular reaction generally requires multi-step synthesis of the designed substrates and thus limits the structures of the products. Consequently, there is a great demand to develop palladium-catalyzed intermolecular dearomatization of phenol derivatives by cross-coupling with simple electrophiles such as aryl halides. The challenge for such a reaction process is obvious, as phenols and aryl halides are known to undergo a C–O bond-forming reaction in the presence of a palladium catalyst (Eq. (1)).^[9,10] Therefore, to avoid the O-arylation process will be key for a highly efficient palladium-catalyzed intermolecular cross-coupling-type dearomatization of phenol derivatives. As naphthols display relatively weak aromaticity compared to phenols, we envisaged that the utilization of naphthols might facilitate the proposed palladium-catalyzed cross-coupling-type dearomatization reaction. Such an intermolecular reaction would provide easy access to the naphthalenone scaffold. Previous limited reports on intermolecular dearomative arylation of naphthol or phenol derivatives include the utilization of stoichiometric aryl lead or aryl bismuth reagents,^[11,12] hypervalent-iodine-mediated dearomatizing phenylation,^[13] and the oxidation of phenols by stoichiometric oxidant^[14] or an

electrochemical method.^[15] Herein, we report the first Pd^0 -catalyzed intermolecular arylative dearomatization of β -naphthols (**1**) with aryl halides, which constructs 2-naphthalenones bearing an all-carbon quaternary stereogenic center at the α -position, in excellent yields and with high chemoselectivity (Eq. (2)).

Buchwald and Hartwig's work:



This work:



The study was launched by utilizing 1,3-dimethyl-2-naphthol (**1a**) and bromobenzene (**2a**) as the model substrates to examine different ligands with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ as a palladium precursor. The results are summarized in Table 1. None of the desired dearomatized product was obtained when Buchwald-type ligand XPhos (**L1**)^[16] and *rac*-Feringa ligand (**L2**) were used (Table 1, entries 1 and 2), while the utilization of SIPr-HBF₄ (**L3**) and (di-*t*-Bu)XPhos (**L4**)^[16] gave trace amounts of product (**3aa**; Table 1, entries 3 and 4). Fortunately, with ferrocenyl dialkylphosphine Q-Phos (**L5**)^[17] as the ligand, the arylative dearomatization proceeded smoothly, with good conversion and excellent chemoselectivity (73 % yield, **3aa/4aa** = 20/1; Table 1, entry 5). Subsequently, several bases were examined (Table 1, entries 6–9). To our delight, stronger alkali base, such as Cs_2CO_3 , could improve the conversion without affecting the chemoselectivity, and the desired dearomatized product (**3aa**) was obtained in 92 % isolated yield (Table 1, entry 7). Arene-type solvents, such as fluorobenzene and *o*-xylene, could also give satisfactory yields (Table 1, entries 10 and 11). Notably, temperature plays an important role. The reaction at 60 °C was sluggish, and the reaction at 120 °C led to an increase of the O-arylation side product (Table 1, entries 14 and 15). Therefore, the optimized conditions were obtained as the following: $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (2.5 mol %), Q-Phos (**L5**; 7.5 mol %), and Cs_2CO_3 (1.5 equiv) in toluene at 80 °C (Table 1, entry 7).

Subsequently, various β -naphthols (**1a–11**) were reacted with bromobenzene to examine the generality of the novel dearomatization under the optimized reaction conditions (Table 2). It was found that the substituents at the 1- and 3-positions of 2-naphthol are of great importance. When the

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Table 1: Optimization of the reaction conditions.^[a]

Entry	Ligand	Base	Solvent	t [h]	3 aa Yield [%] ^[b]	3 aa:4 aa
1	L1	K ₂ CO ₃	toluene	10	0	ND
2	L2	K ₂ CO ₃	toluene	10	0	ND
3	L3	K ₂ CO ₃	toluene	10	trace	ND
4	L4	K ₂ CO ₃	toluene	10	trace	< 1:20 ^[c]
5	L5	K ₂ CO ₃	toluene	10	80 (73 ^[d])	20:1
6	L5	Na ₂ CO ₃	toluene	10	trace	ND
7	L5	Cs ₂ CO ₃	toluene	6	> 99 (92 ^[d])	> 20:1
8	L5	K ₃ PO ₄	toluene	10	73	> 20:1
9	L5	^t BuOK	toluene	10	24	ND
10	L5	Cs ₂ CO ₃	PhF	15	95	> 20:1
11	L5	Cs ₂ CO ₃	<i>o</i> -xylene	6	99	> 20:1
12	L5	Cs ₂ CO ₃	DCE	2	12	ND
13	L5	Cs ₂ CO ₃	dioxane	15	14	> 20:1
14 ^[e]	L5	Cs ₂ CO ₃	toluene	22	44	> 20:1
15 ^[f]	L5	Cs ₂ CO ₃	toluene	2	80	13:1

[a] Reaction conditions: **1a** (0.2 mmol), [Pd(C₃H₅)Cl]₂ (0.005 mmol), ligand (0.015 mmol), **2a** (0.3 mmol), base (0.3 mmol) in solvent (1.0 mL), 80 °C. [b] Determined by ¹H NMR using CH₂Br₂ (0.2 mmol) as an internal standard. [c] Only etherified product was obtained in 25 % NMR yield. [d] Isolated yield. [e] Temperature was 60 °C. [f] Temperature was 120 °C.

Table 2: The reaction substrate scope: Naphthols.^[a]

Entry	1, R ¹ , R ² , R ³	3:4 ^[b]	Yield of 3 [%] ^[c]
1	1a , Me, Me, H	> 20:1	3aa , 92
2	1b , Et, Me, H	> 20:1	3ba , 93
3	1c , CH ₂ CH ₂ Ph, Me, H	> 20:1	3ca , 99
4	1d , Me, Et, H	> 20:1	3da , 91
5	1e , Me, Bn, H	10:1	3ea , 73
6	1f , Me, Me, 6-Ph	> 20:1	3fa , 92
7	1g , Me, Me, 6-Me	> 20:1	3ga , 94
8	1h , Me, Me, 7-Ph	> 20:1	3ha , 92
9	1i , Me, Me, 7-Me	> 20:1	3ia , 91
10	1j , Me, H, H	4:1	3ja , 48 ^[d]
11	1k , Ph, Me, H	ND	3ka , 9 ^[e]
12	1l , CO ₂ Me, Me, H	ND	3la , trace

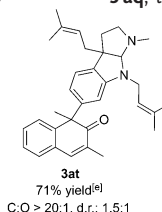
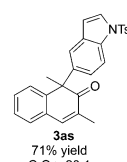
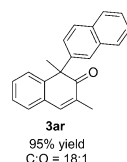
[a] Reaction conditions: **1** (0.2 mmol), [Pd(C₃H₅)Cl]₂ (0.005 mmol), Q-Phos (0.015 mmol), **2a** (0.3 mmol), Cs₂CO₃ (0.3 mmol) in toluene (1.0 mL), 80 °C. [b] Determined by ¹H NMR. [c] Isolated yield. [d] **1j** (0.2 mmol), [Pd(C₃H₅)Cl]₂ (0.005 mmol), Q-Phos (0.015 mmol), **2a** (0.3 mmol), K₂CO₃ (0.3 mmol) in toluene (1.0 mL), 80 °C. [e] NMR yield, determined by ¹H NMR using CH₂Br₂ (0.2 mmol) as an internal standard.

substituents were both alkyl groups, the corresponding 2-naphthols underwent dearomatization smoothly, in good to excellent yields and chemoselectivity (Table 2, entries 2–5). However, 1-methyl-2-naphthol (**1j**) was less reactive; only 48 % yield of the desired product was obtained and some starting material remained. Additionally, the presence of a phenyl group (**1k**) or an electron-withdrawing group such as CO₂Me (**1l**) at the 1-position could inhibit the dearomatization (Table 2, entries 11 and 12). Overall, electron-rich β-naphthols facilitate the dearomatization, as 1,3-dimethyl-2-naphthol derivatives bearing 6-Ph (**1f**), 6-Me (**1g**), 7-Ph (**1h**), and 7-Me (**1i**) groups all led to their corresponding dearomatized products in excellent yields and with high chemoselectivity (91–94 % yields, **3/4** > 20/1; Table 2, entries 6–9).

Subsequently, the reactions of naphthol **1a** with various aryl halides (**2**) were examined. As shown in Table 3, when different halides such as Cl (**2b**) and I (**2c**) were tested, the reactions occurred smoothly with excellent chemoselectivity (> 20:1), but in slightly decreased yields (Table 3, entries 2 and 3). After that, the substituent effect of aryl bromides was carefully examined. Aryl bromides bearing an electron-

Table 3: The reaction substrate scope: Aryl halides.^[a]

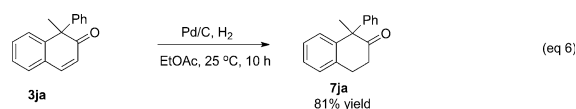
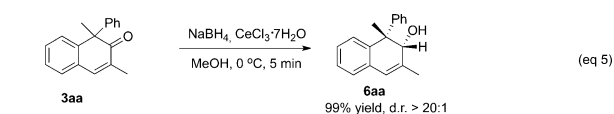
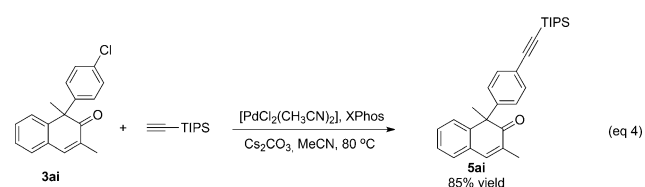
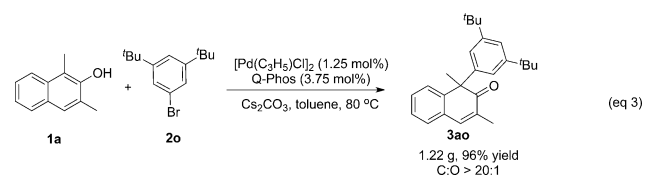
Entry	2, R ¹ , X	3:4 ^[b]	Yield of 3 [%] ^[c]
1	2a , H, Br	> 20:1	3aa , 92
2	2b , H, Cl	> 20:1	3ab , 81
3	2c , H, I	> 20:1	3ac , 84
4	2d , 4-Me, Br	> 20:1	3ad , 93
5	2e , 4-OMe, Br	> 20:1	3ae , 95
6	2f , 4- ^t Bu, Br	> 20:1	3af , 99
7	2g , 4- ⁿ Bu, Br	> 20:1	3ag , 91
8	2h , 4-Ph, Br	18:1	3ah , 93
9	2i , 4-Cl, Br	> 20:1	3ai , 90
10	2j , 4-F, Br	> 20:1	3aj , 86
11	2k , 4-CF ₃ , Br	4:1	3ak , 75
12	2l , 4-CO ₂ Me, Br	2.1:1	3al , 62
13	2m , 4-NO ₂ , Br	1:2.1	3am , 31
14	2n , 3-Me, Br	> 20:1	3an , 91
15	2o , 3,5-(^t Bu) ₂ , Br	> 20:1	3ao , 99
16	2p , 3-F, Br	> 20:1	3ap , 92
17	2q , 2-Me, Br	< 1:20 ^[d]	3aq , trace



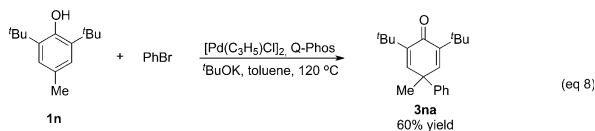
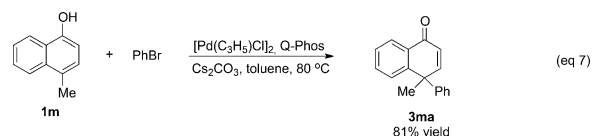
[a] Reaction conditions: **1a** (0.2 mmol), [Pd(C₃H₅)Cl]₂ (0.005 mmol), Q-Phos (0.015 mmol), **2** (0.3 mmol), Cs₂CO₃ (0.3 mmol) in toluene (1.0 mL), 80 °C. [b] Determined by ¹H NMR. [c] Isolated yield. [d] Only etherified product was obtained in 20% NMR yield. [e] **1a** (0.1 mmol), [Pd(C₃H₅)Cl]₂ (0.005 mmol), Q-Phos (0.015 mmol), **2t** (0.1 mmol), Cs₂CO₃ (0.15 mmol) in toluene (1.0 mL), 80 °C.

donating substituent or halide (Me, OMe, ^tBu, ⁿBu, Ph, Cl, F) at the *para*-position could be tolerated to give their desired products in excellent yields and with high chemoselectivity (86–99 % yields, **3/4**: 18/1–>20/1; Table 3, entries 4–10). However, aryl bromides bearing a strong electron-withdrawing substituent (CF₃, CO₂Me, NO₂) at the *para*-position led to an increase of the *O*-arylation side product (Table 3, entries 11–13). More *O*-arylation product is formed when the substrate bearing a stronger electron-withdrawing substituent is employed. Aryl bromides bearing a *meta*-substituent also participated smoothly in the dearomative cross-coupling reaction in excellent yields and with high chemoselectivity (Table 3, entries 14–16). Probably as a result of the steric effect, the reaction of *ortho*-substituted aryl bromide (**2q**) only gave *O*-arylation product in 20 % yield (determined by NMR spectroscopy; Table 3, entry 17). Pleasingly, when more complicated aryl bromides were tested, such as 2-bromonaphthalene and 5-bromoindole, these reactions afforded dearomatized products **3ar** and **3as** in 95 % and 71 % yield, respectively, with excellent chemoselectivity. The structure of **3ar** was confirmed by an X-ray crystallographic analysis. It is worth noting that natural product flustramine B^[18] could be employed as a coupling partner to give dearomatized product **3at** in 71 % yield.

To further demonstrate the utility of this method, a gram-scale reaction and transformations of the 2-naphthalenone products have been carried out. The intermolecular arylative dearomatization of **1a** with 3,5-di-*tert*-butylbromobenzene (**2o**) in a 3.5 mmol scale gave the desired product **3ao** in 96 % yield and excellent chemoselectivity (**3ao:4ao** > 20:1) while the catalyst loading could be further reduced to 1.25 mol % [Eq. (3)]. Dearomatized product **3ai** could undergo the Sonogashira coupling reaction with ethynyltriisopropylsilane to afford **5ai** in 85 % yield [Eq. (4)]. Additionally, the ketone group of product (**3aa**) could be selectively transformed to an alcohol (**6aa**) in 99 % yield (d.r. > 20:1; Eq. (5)) under Luche reduction conditions, and the double bond of **3ja** could be hydrogenated to form **7ja** in 81 % yield [Eq. (6)].

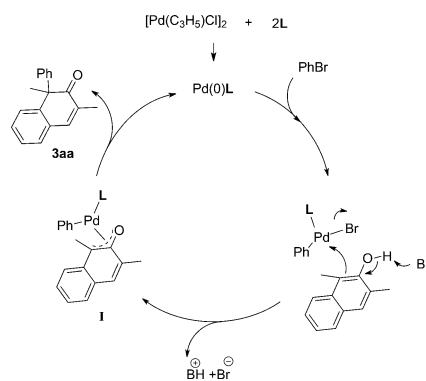


To our delight, 4-methyl-1-naphthol (**1m**) underwent dearomatization to afford benzoenone (**3ma**) in 81 % yield [Eq. (7)], while 2-methyl-1-naphthol underwent a Friedel–Crafts-type reaction at the *para*-position under standard reaction conditions (for details, see the Supporting Information). Moreover, substituted phenol (**1n**) is also a suitable substrate to afford dienone (**3na**) in 60 % yield under slightly forced conditions [Eq. (8)], while 2,4,6-trimethylphenol underwent an *O*-arylation process to afford the ether product (for details, see the Supporting Information).



Preliminary mechanistic investigation revealed that the dearomatization product and the *O*-arylation product cannot be interconverted with each other under standard conditions (for details, see the Supporting Information). A catalytic cycle was proposed as depicted in Scheme 1. The in situ formed Pd⁰ species undergoes oxidative addition across the C–Br bond in bromobenzene, affording a phenyl palladium species. Assisted by base, the 1,3-dimethyl-2-naphthol proceeds ligand exchange to form oxo- π -allylic palladium intermediate **I**, which then undergoes reductive elimination to afford product **3aa** and finish the catalytic cycle.

In summary, we have developed the first palladium-catalyzed intermolecular arylative dearomatization of



Scheme 1. Proposed catalytic cycle for palladium-catalyzed arylative dearomatization of naphthols.

β -naphthols with aryl halides to construct 2-naphthalenones bearing an all-carbon quaternary stereogenic center at the α -position, in excellent yields and with high chemoselectivity. It was found that Q-Phos could facilitate the dearomatization of β -naphthols while avoiding an *O*-arylation process. Further studies on the reaction mechanism and development of catalytic asymmetric reactions are currently under investigation.

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Keywords: cross-coupling · dearomatization · homogeneous catalysis · naphthol · palladium

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