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Letter

Ni-Catalyzed Allylic Dearomatization Reaction of β-Naphthols with Allylic Alcohols

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01109

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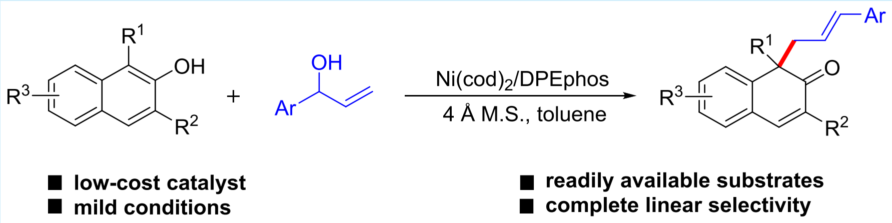
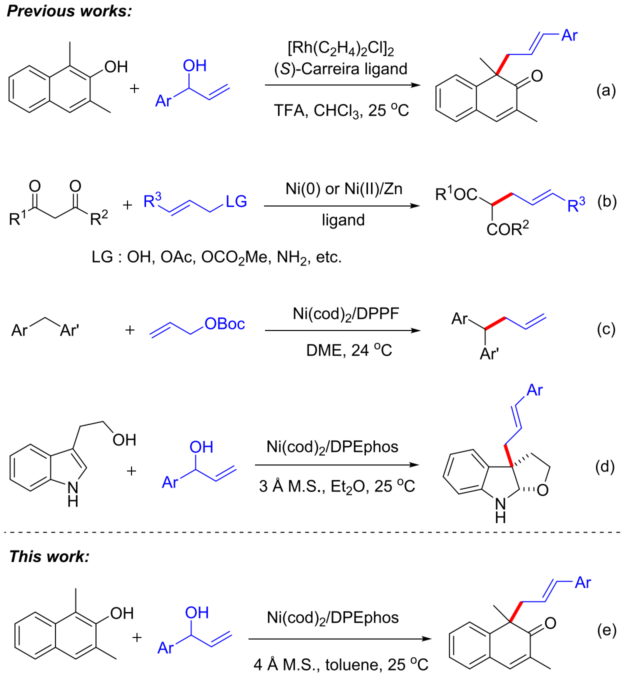


ABSTRACT: Ni-catalyzed intermolecular allylic dearomatization reaction of β-naphthols with allylic alcohols was achieved. By utilizing Ni(cod)$_2$ as a catalyst precursor, DPEphos as a ligand and 4 Å molecular sieves as additives, the dearomatization reaction of β-naphthols with aryl allylic alcohols proceeded smoothly under mild conditions, affording the desired β-naphthalenone products bearing a quaternary carbon center in moderate to good yields with excellent linear selectivity.

Naphthols are inexpensive and readily available materials, and their dearomatized motifs are frequently encountered in numerous biologically active compounds and natural products.[1] Therefore, many efforts have been devoted to the transition-metal catalyzed dearomatization of naphthols in the past decade.[2] To date, Pd-catalyzed,[3] Ir-catalyzed,[4] and Rh-catalyzed[5] allylic dearomatization reactions of naphthols have been well-developed, offering a facile and straightforward access to naphthalenones (Scheme 1a). Thus, developing sustainable alternatives to achieve transition-metal-catalyzed allylic dearomatization reactions remains to be highly desirable. In this context, nickel catalysis is an attractive choice, because of the abundance and low cost of nickel and its unique reaction properties.[6]

Contrast to the rapid development of Pd-catalyzed allylic substitution reactions, in which soft nucleophiles are generally employed,[7] Ni-catalyzed allylic substitution reactions progressed much more slowly over the past decades. Most of pioneering works on Ni-catalyzed reactions generally involved "hard" nucleophiles, such as Grignard reagents[8] and other organometallics.[9] However, Ni-catalyzed allylic substitution reactions with "soft" nucleophiles are rather limited, as these reactions usually require more harsh reaction conditions or highly activated substrates.[10] Since the Mortreux group introduced dimethyl malonate type "soft" nucleophile into Ni-catalyzed allylic substitution reactions,[11] the application of various activated nucleophiles has been successfully developed. For instance, allylic substitution reactions involving malonates,[12] β-keto esters,[13] and diarylmethane[14] were investigated (see Schemes 1b and 1c). Recently, we introduced tryptophols and tryptamines as nucleophiles in Ni-catalyzed allylic substitution reaction, affording dearomatized 3-cinnamyl

Scheme 1. Ni-Catalyzed Allylic Substitution Reactions

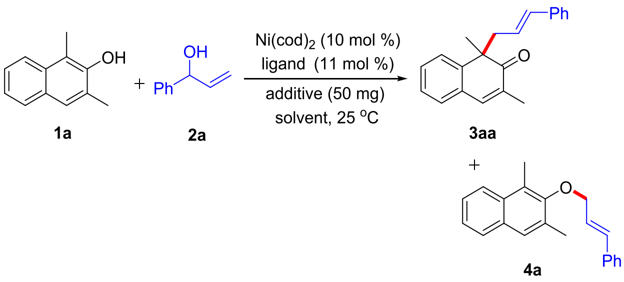


Received: March 26, 2020

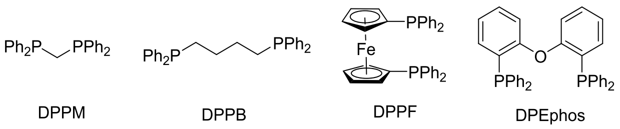
indolines in moderate to good yields (Scheme 1d).[15] In this reaction, Ni(cod)$_2$/DPEphos, a commercially available catalytic system, was found to be efficient for the synthesis of pyrrolidinoindolines and tetrahydrofuranoindolines. The successful application of nickel/diphosphine system encouraged us to further explore other Ni-catalyzed allylic dearomatization reactions. Herein, we report a Ni-catalyzed intermolecular allylic dearomatization of β-naphthols with allylic alcohols, providing β-naphthalenones with a quaternary carbon stereocenter in moderate to good yields (Scheme 1e).

Initially, 1,3-dimethyl-2-naphthol (**1a**) and phenyl vinyl carbinol (**2a**) were chosen as the model substrates (Table 1).

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3aa** **4a**



DPPM DPPB DPPF DPEphos

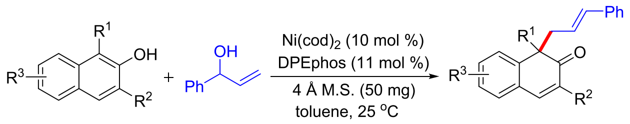
entry	ligand	solvent	additive	3aa/4a[b]	NMR yield[c] of 3aa (%)
1	PPh$_3$	Et$_2$O	3 Å M.S.	–	N.R.[d]
2	DPPM	Et$_2$O	3 Å M.S.	–	N.R.[d]
3	DPPB	Et$_2$O	3 Å M.S.	>19:1	39
4	DPPF	Et$_2$O	3 Å M.S.	>19:1	60
5	DPEphos	Et$_2$O	3 Å M.S.	>19:1	82 (79[e])
6	DPEphos	THF	3 Å M.S.	>19:1	20
7	DPEphos	1,4-dioxane	3 Å M.S.	>19:1	27
8	DPEphos	CH$_3$CN	3 Å M.S.	>19:1	25
9	DPEphos	CH$_2$Cl$_2$	3 Å M.S.	–	N.R.[d]
10	DPEphos	toluene	3 Å M.S.	>19:1	83 (82[e])
11	DPEphos	toluene	4 Å M.S.	>19:1	93 (90[e])
12	DPEphos	toluene	5 Å M.S.	>19:1	90 (87[e])
13[f]	DPEphos	toluene	4 Å M.S.	>19:1	68
14[g]	DPEphos	toluene	4 Å M.S.	–	N.R.[d]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), Ni(cod)$_2$ (10 mol %), ligand (11 mol %), additive (50 mg) in solvent (2 mL) at 25 °C for 48 h. [b] Determined by ^{1}H NMR analysis. [c] Determined by ^{1}H NMR of the crude reaction mixture using dibromomethane as an internal standard. [d] N.R. = no reaction. [e] Isolated yield. [f] 5 mol % Ni(cod)$_2$, 5.5 mol % DPEphos. [g] 2 mol % Ni(cod)$_2$, 2.2 mol % DPEphos.

In the presence of 10 mol % Ni(cod)$_2$ and 50 mg 3 Å molecular sieves in Et$_2$O at 25 °C,[15] the reaction did not work when PPh$_3$ or DPPM was used as the ligand (Table 1, entries 1 and 2). To our delight, utilization of DPPB and DPPF could give the desired product **3aa** in 39% and 60% NMR yields, respectively (Table 1, entries 3 and 4). DPEphos was found to be the most efficient ligand, giving **3aa** in 82% NMR yield (Table 1, entry 5). Subsequently, the solvent effect was investigated. Tetrahydrofuran (THF), 1,4-dioxane, and CH$_3$CN were not effective solvents, and only a small amount of **3aa** was formed (Table 1, entries 6–8, 20%–27% NMR yields), whereas the reaction in CH$_2$Cl$_2$ was completely inhibited (Table 1, entry 9). Pleasingly, the reaction in toluene proceeded smoothly, and **3aa** was obtained in 82% yield (Table 1, entry 10). Among the solvents tested, toluene proved to be the best one. Different molecular sieves were examined, and the yield of **3aa** was slightly increased to 90% and 87% (Table 1, entries 11 and 12) by utilizing 4 and 5 Å molecular sieves, respectively. With 4 Å molecular sieves as the additive, the catalyst loading was then tested. When the catalyst loading was reduced to 5 and 2 mol %, 68% NMR yield and a trace amount of **3aa** were obtained, respectively (Table 1, entries 13 and 14). In addition, various chiral monodentate and bidentate phosphine ligands were systematically tested. Unfortunately, poor enantioselective control was achieved (for details, see the Supporting Information). Thus, the optimal reaction conditions were established as follows: Ni(cod)$_2$ (10 mol %), DPEphos (11 mol %) and 4 Å molecular sieves (50 mg) in toluene at 25 °C (Table 1, entry 11).

With the optimized conditions in hand, the reactions of various β-naphthols **1** and phenyl vinyl carbinol **2a** were performed. As shown in Table 2, a variety of 1- and 3-alkyl substituted β-naphthols afforded their corresponding products in moderate to good yields (**3aa**–**3ca**, **3ea**–**3fa**: 64%–90%). Unfortunately, the reaction of 3-chloro-β-naphthol **1d** failed to afford the dearomatized product (Table 2, entry 4). In addition, 1-phenyl β-naphthol **1g** only gave **3ga** in 10% NMR yield (Table 2, entry 7). These results indicated that the electronic and steric factors had a significant impact on the reactivity. Besides 1- and 3-alkyl substituents, 6-OMe, 6-Ph, 7-Me, 7-OMe, and 7-Ph groups could be well-tolerated, demonstrating the wide substrate scope of this reaction (Table 2, entries 8–12, **3ha**–**3la**: 56%–86% yields).

Table 2. Scope of the Substituted β-Naphthols[a]



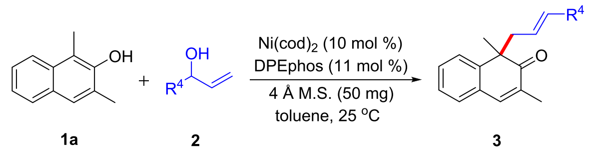
1 **2a** **3**

entry	1, R^1, R^2, R^3	reaction time, t (h)	3, yield (%)[b]
1	**1a**, Me, Me, H	36	**3aa**, 90
2	**1b**, Et, Me, H	48	**3ba**, 66
3	**1c**, Me, Bn, H	60	**3ca**, 69
4	**1d**, Me, Cl, H	72	N.R.[c]
5	**1e**, Me, H, H	36	**3ea**, 81
6	**1f**, Et, H, H	48	**3fa**, 64
7	**1g**, Ph, H, H	72	**3ga**, 10[d]
8	**1h**, Me, H, 6-OMe	36	**3ha**, 77
9	**1i**, Me, H, 7-Me	36	**3ia**, 77
10	**1j**, Me, Me, 6-Ph	36	**3ja**, 78
11	**1k**, Me, Me, 7-OMe	36	**3ka**, 86
12	**1l**, Me, Me, 7-Ph	72	**3la**, 56

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.24 mmol), Ni(cod)$_2$ (10 mol %), DPEphos (11 mol %), 4 Å M.S. (50 mg) in toluene (2 mL) at 25 °C. [b] Isolated yield. [c] N.R. = no reaction. [d] Determined by ^{1}H NMR of the crude reaction mixture using dibromomethane as an internal standard.

Next, various substituted allylic alcohols were tested for this reaction (Table 3). Allylic alcohols with either electron-withdrawing (F, Cl) or electron-donating (CH$_3$, OCH$_3$)

Table 3. Scope of Allylic Alcohols[a]



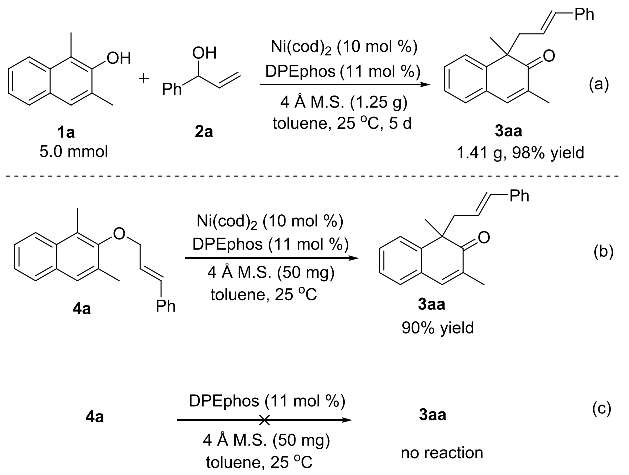
entry	**2**, R^4	reaction time, *t* (h)	**3**, yield[b] (%)
1	**2a**, Ph	36	**3aa**, 90
2	**2b**, 2-Me-C_6H_4	36	**3ab**, 70
3	**2c**, 2-OMe-C_6H_4	36	**3ac**, 60
4	**2d**, 2−F-C_6H_4	72	**3ad**, 67
5	**2e**, 2-NHAc-C_6H_4	72	**3ae**, 40
6	**2f**, 3-Me-C_6H_4	36	**3af**, 84
7	**2g**, 3−F-C_6H_4	48	**3ag**, 75
8	**2h**, 4-Me-C_6H_4	36	**3ah**, 83
9	**2i**, 4-OMe-C_6H_4	36	**3ai**, 87
10	**2j**, 4−Cl-C_6H_4	72	**3aj**, 34
11	**2k**, 4−F-C_6H_4	72	**3ak**, 67
12	**2l**, 2-furyl	48	**3al**, 84
13	**2m**, 2-thienyl	48	**3am**, 77
14	**2n**, 2-naphthyl	48	**3an**, 74
15	**2o**, isobutyl	72	N.R.[c]
16	**2p**, cyclohexyl	72	N.R.[c]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), Ni(cod)$_2$ (10 mol %), DPEphos (11 mol %), 4 Å M.S. (50 mg) in toluene (2 mL) at 25 °C. [b] Isolated yield. [c] N.R. = no reaction.

groups on the phenyl ring were suitable substrates, the corresponding dearomatized products **3aa**−**3an** were obtained in 34%−90% yields. Moreover, 2-furyl, 2-thienyl, and 2-naphthyl allylic alcohols underwent the allylic dearomatization reaction smoothly, delivering **3al**−**3an** in good yields (Table 3, entries 12−14, 74%−84%). However, the reactions of aliphatic allylic alcohols such as 5-methylhex-1-en-3-ol **2o** and 1-cyclohexylprop-2-en-1-ol **2p** failed to afford the dearomatized products (Table 3, entries 15 and 16). Notably, the reactions for all substrates exclusively afforded the corresponding linear products as (*E*)-isomers.

To further demonstrate the practicality of this method, the reaction of **1a** with **2a** was performed on a 5 mmol scale (Scheme 2a). The reaction was completed after 5 days, giving **3aa** (1.41 g) in 98% yield.

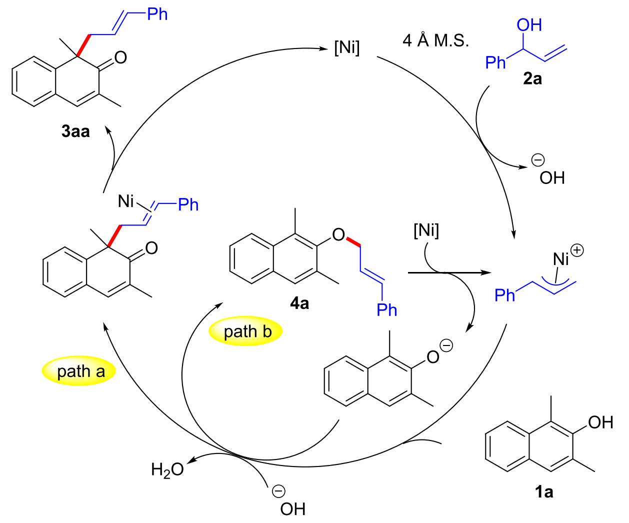
Scheme 2. Gram-Scale Reaction and Mechanistic Study



To gain insights into the reaction mechanism, preliminary experiments were performed. The ether **4a** was subjected to the standard conditions, and *α*-C allylated dearomatization product **3aa** was obtained in 90% yield (Scheme 2b). However, this reaction did not work in the absence of Ni(cod)$_2$ (Scheme 2c). Notably, a small amount of **4a** was identified by HPLC analysis. In addition, the conversion rate of **4a** to **3aa** was found to be higher than that of the model reaction of **1a** with **2a** (for details, see the Supporting Information). Therefore, it is very likely that the etherification product **4a** is a competent intermediate.

On the basis of these experimental results, a plausible catalytic cycle was proposed (Scheme 3).[3b,16] The direct allylic alkylation reaction at the *α*-C of naphthol is a feasible process (path a); however, an alternative pathway involving O-allylation and subsequent *α*-C alkylation cannot be ruled out. First, in the presence of the acidic molecular sieves, the *π*-allyl nickel species is generated by the reaction of allylic alcohol with Ni(0). Subsequently, nucleophilic attack by the *α*-C of naphthol or phenolic hydroxyl group affords C-allylated product **3aa** (path a) or O-allylated product **4a** (path b). The C−O bond of **4a** can also be cleaved by Ni(0) to give the enolate and *π*-allyl nickel species, which undergo the *α*-C alkylation reaction to afford the dearomatization product **3aa**.

Scheme 3. Proposed Reaction Mechanism



In conclusion, we have demonstrated an efficient Ni-catalyzed allylic dearomatization of *β*-naphthols with various allylic alcohols. The reaction proceeded well in the presence of readily available Ni(cod)$_2$/DPEphos catalyst under mild conditions. *β*-Naphthalenones containing an all-carbon-substituted quaternary stereocenter could be obtained in moderate to good yields. Further studies on asymmetric Ni-catalyzed allylic dearomatization reactions are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01109.

Experimental procedures and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Key R&D Program of China (No. 2016YFA0202900), NSFC (Nos. 21821002, 91856201, 21961132002), and the CAS (Nos. XDB20000000, QYZDY-SSW-SLH012) for generous financial support. S.-L.Y. acknowledges the support from the Tencent Foundation, through the XPLORER PRIZE.

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