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Palladium-catalyzed dearomative 1,4-difunctionalization of naphthalenes†

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A highly diastereoselective dearomatization of naphthalenes via a Pd-catalyzed 1,4-difunctionalization reaction is described. In the presence of a commercially available palladium precursor and ligand, intramolecular dearomative Heck-type insertion provides π -allylpalladium intermediates which are readily captured by a series of nucleophiles in excellent yields (up to 99%). This reaction features mild conditions, broad substrate scope, and useful transformations of the products.

Introduction

The difunctionalization of alkenes is widely recognized as a powerful approach to generate significant molecular complexity from simple chemical feedstock. In particular, Pd-catalyzed difunctionalization of 1,3-dienes, which introduces two functional groups across the conjugated C=C double bonds, has witnessed significant progress in the past decade. Mechanistically, Pd(II) complexes, usually generated from the oxidative addition of Pd(0) precursors, have been employed to achieve these reactions through Heck insertion to form a π -allylpalladium species. The subsequent regionselective nucleophilic attacks afford 1,2- or 1,4-addition-like products (Scheme 1a). However, the scope of these transformations was in general limited to structurally simple dienes and furans.

In line with our continuous interest in catalytic dearomatization reactions,⁶ we envisioned that the formal "conjugated diene" structure of the phenyl ring might serve as the equivalent of 1,3-dienes. However, the dearomatization of electronically unbiased aromatic compounds such as naphthalenes and benzenes remained challenging,⁷ due to the generally higher aromatic stabilization energies of plain arenes compared with their heteroaromatic counterparts (36 kcal mol⁻¹ for benzene and 22 kcal mol⁻¹ for pyrrole).⁶ Therefore, the translation of Pd-catalyzed difunctionalization of 1,3-dienes to aromatic systems would open a new window for the dearomatization of non-activated arenes.

Inspired by the recent developments in Pd-catalyzed dearomative Heck reactions⁸ that are terminated by the nucleophilic attack on alkylpalladium intermediates (Scheme 1b),⁹ we realized

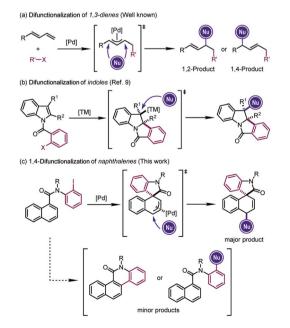
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that the π -allylpalladium intermediates formed from the Hecktype insertion into the naphthalene ring might also be captured using external nucleophiles, furnishing the dearomative 1,4-difunctionalization of naphthalenes (Scheme 1c). The successful execution of this reaction design relied on the judicious selection of the catalytic system which could overcome the thermodynamic disadvantage of the dearomatization process and at the same time avoid the competitive C–H activation or direct cross-coupling reactions. Herein we report our results from this study.

Results and discussion

We began our investigation by studying the 1,4-difunctionalization of N-(2-iodophenyl)-N-methyl-1-naphthamide (1a) with



Scheme 1 Difunctionalization of 1,3-dienes, indoles and naphthalenes.

dimethyl malonate (2a) (Table 1). Firstly, we tested different ligands in the presence of PdCl₂ (10 mol%), NaH (2.0 equiv.), and Ag₃PO₄ (1.0 equiv.) in DMA at 100 °C. When BINAP (L1), BINAP(O) (L2), and Feringa phosphoramidite (rac-L3) were used as the ligand respectively, the dearomatized product 3a was obtained as a single diastereomeric isomer in good yields (67-90%) (entries 1-3), whose structure and relative configuration were confirmed by X-ray crystallographic analysis. The relative configuration of 3a revealed that the in situ formed π -allylpalladium intermediate was attacked by the nucleophile via an outer sphere mechanism. On the other hand, the reaction with the PHOX ligand (L4) was sluggish (entry 4). Subsequently, different solvents were examined by using rac-L3 as the ligand (entries 5-8). DMA was found to be the optimal one among those tested. In particular, the desired reaction was prohibited significantly when ^tBuOH was employed (entry 6). Next, the effects of various bases were examined (entries 9-12). This revealed that 3a could be obtained in moderate yields by using K₂CO₃ or K₃PO₄, while the target product was not observed when 1,2,2,6,6-pentamethylpiperidine (PMP) or ^tBuOK was

Table 1 Optimization of the reaction conditions^a

Entry	Ligand	Base	Solvent	$\mathbf{1a}^{b}\left(\%\right)$	$3\mathbf{a}^{b}\left(\%\right)$
1 ^c	L1	NaH	DMA	_	79
2^c	L2	NaH	DMA	15	67
3	rac -L3 d	NaH	DMA	_	$90 (90^e)$
4^c	L4	NaH	DMA	44	43
5	rac -L3 d	NaH	Toluene	69	22
6	rac -L3 d	NaH	^t BuOH	Quant.	Trace
7	rac -L3 d	NaH	DCE	63	36
8	rac -L3 d	NaH	Dioxane	52	51
9	rac -L3 d	K_2CO_3	DMA	43	46
10	rac -L3 d	K_3PO_4	DMA	51	29
11	rac -L3 d	PMP^f	DMA	Quant.	Trace
12	rac -L3 d	^t BuOK	DMA	66	Trace
13^g	rac -L3 d	NaH	DMA	66	27
14^h	rac -L3 d	NaH	DMA	84	8
15^i	rac -L3 d	NaH	DMA	77	5
16 ^j	rac -L3 d	NaH	DMA	_	$97 (95^e)$

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), PdCl₂ (0.02 mmol), ligand (0.04 mmol), base (0.4 mmol), and Ag₃PO₄ (0.2 mmol) in solvent (1.0 mL) at 100 °C. ^b Yield determined by ¹H NMR using CH₂Br₂ (0.2 mmol) as an internal standard. ^c Ligand (0.02 mmol). ^d rac-L3: ($R_{\rm a}$ R, R + $S_{\rm a}$ S, $S_{\rm s}$): ($S_{\rm a}$ R, R + $R_{\rm a}$ S, $S_{\rm s}$) = 1 : 4. ^e Isolated yield. ^f PMP: 1,2,2,6,6-pentamethylpiperidine. ^g AgOTf as the silver salt. ^h AgNTf₂ as the silver salt. ⁱ AgBF₄ as the silver salt. ^j Sodium salt of **2a** (pre-prepared by mixing NaH (0.4 mmol) and **2a** (0.4 mmol) in DMA at room temperature for 0.5 h), PdCl₂ (0.01 mmol), and rac-L3 (0.02 mmol).

employed. Surprisingly, the judicious choice of silver salts was quite critical to this reaction. Among those tested, Ag₃PO₄ provided the optimal reaction outcomes. Other commonly used silver salts including AgOTf, AgNTf₂, and AgBF₄ were ineffective (entries 13–15). Finally, the optimal yield of **3a** (95%) was obtained by using a pre-prepared sodium salt of **2a** with lower catalyst loading (5 mol%) (entry 16).

With the optimal conditions in hand, we surveyed the generality of this novel 1,4-difunctionalization by allowing various naphthalene derivatives 1 to react with sodium salts of dialkyl malonates 2 (Table 2). When the methyl group on the nitrogen tether of 1 was changed to isopropyl or benzyl groups, the desired products 3b and 3c were obtained in good yields (82-86%). The substrates bearing an electron-donating group (Me and OMe) or halide (F, Cl, and Br) at the para position of the phenyl ring led to 3d-3h in 75-98% yields. The good tolerance with halides would offer a handle on subsequent transformations. In contrast, when an electron-withdrawing group (CF₃, CO₂Me, and CN) was incorporated into the aryl iodide moiety, the corresponding products (3i, 3j, 3l) were formed in moderate yields (40-51%). Notably, an ortho substituent on the phenyl ring was well tolerated, affording the dearomatized product 3m in 80% yield. Naphthalene derivatives bearing a substituent at the C6 position furnished the products 3n-3p in reasonable yields (39-82%). It is worth noting that 3a could be obtained in 75% yield by using N-(2-bromophenyl)-N-methyl-1-

Table 2 Substrate scope of naphthalenes and malonic diesters^a

 a 1 (0.2 mmol), 2 (0.4 mmol, pre-prepared from malonic ester with NaH), PdCl $_2$ (0.01 mmol), rac-L3 (0.02 mmol), and Ag $_3\text{PO}_4$ (0.2 mmol) in DMA (1.0 mL) at 100 °C. b Pre-synthesized PdCl $_2$ –BINAP complex (0.01 mmol) was used. c N-(2-Bromophenyl)-N-methyl-1-naphthamide was used at 120 °C. d PdCl $_2$ (0.02 mmol) and rac-L3 (0.04 mmol) at 120 °C.

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naphthamide as the substrate and BINAP as the ligand. In addition, when diethyl malonate or dibenzyl malonate was utilized as the nucleophile, the desired products 3q and 3r were obtained with good yields (81-87%). The dearomatized product 3s bearing two all-carbon quaternary stereocenters could be afforded in 28% yield. The low yield probably resulted from the unfavorable steric hindrance in the second step.

Next, different 1,3-diketones were explored under slightly modified conditions (Table 3). When acetylacetone and 3,5heptanedione were employed as the coupling partners, the corresponding products 4a and 4b were delivered in good yields (67-69%). Notably, cyclic β-diketones were also tolerated, leading to 4c and 4d in moderate yields (42-55%).

The reaction design was successfully applied to the sodium salts of β-ketoesters (Table 4). The reactions of diverse alkyl

Table 3 Substrate scope of 1,3-diketones

^a 1a (0.2 mmol), 2 (0.4 mmol), pre-synthesized PdCl₂-BINAP complex (0.02 mmol), Ag₃PO₄ (0.2 mmol), and Na₂HPO₄·12H₂O (0.4 mmol) in DMA (1.0 mL) at 120 °C.

Substrate scope of β -ketoesters^{a,b} Table 4

^a 1a (0.2 mmol), 2 (0.4 mmol, pre-prepared from β-ketoester with NaH), PdCl₂ (0.01 mmol), rac-L3 (0.02 mmol), and Ag₃PO₄ (0.2 mmol) in DMA (1.0 mL) at 100 °C. b The diastereomeric selectivity originates from the reversal of the relative configuration at the position denoted with an asterisk. ^c PdCl₂ (0.02 mmol), rac-L3 (0.04 mmol).

substituted β-ketoesters furnished the desired products in good to excellent yields (5a-5f, 56-99%). Aryl β-ketoesters also participated smoothly in the reaction, regardless of the electronic properties of the aryl group, delivering 5g-5i in good yields (59–76%). Of particular note is that 2-thienyl and 2-furyl β-ketoesters could be converted to 5i and 5k in moderate to good yields (45-89%).

In addition to β-ketoesters, the esters bearing an electronwithdrawing group (NO₂ and SO₂Ph) at the α-position were proved to be viable participants, leading to 5l and 5m in moderate yields (24-51%) (Scheme 2). Although obtained as a mixture of a pair of diastereoisomers with poor dr values, the products could undergo decarboxylation to deliver pure dearomatized compounds (vide infra).

To further demonstrate the generality of this reaction, we focused on developing the 1,4-difunctionalization with nitrogen-based nucleophiles (Table 5). Various benzyl amines were investigated as the nucleophiles. The corresponding products 6a and 6b could be obtained in excellent yields (97-99%). Moreover, furfurylamine and 2-thiophenemethylamine were also compatible, leading to dearomatized products 6c and 6d in good yields (76-98%). Cyclic secondary amines, such as pyrrolidine, piperidine and morpholine, reacted as the coupling partners to form the tertiary amines 6f-6h in excellent yields (98–99%). Diethylamine and cyclohexylamine also participated in the reaction smoothly, leading to 6e and 6i in excellent yields (88-95%). It is noteworthy that various anilines regardless of electronic properties were also viable reaction partners. The desired products 6k-6m could be delivered in high yields (80-99%). The structure of 6k was determined by X-ray crystallographic analysis. Notably, the reactions of tryptamine and allylamine led to 6j and 6n in low yields. When (R)-1-phenylethylamine was used, 60 was obtained in 96% yield with a 1:1

Preliminary investigations on the enantioselective variants of the dearomative 1,4-difunctionalization reactions of naphthalene derivatives with dimethyl malonate or aniline were performed. Unfortunately, the utilization of a series of chiral ligands did not afford satisfactory asymmetric induction (see the ESI† for details).

To test the practicality of this method, a gram-scale dearomative 1,4-difunctionalization reaction of 1a (4.0 mmol) and aniline with a lower catalyst loading (2.5 mol%) was carried out (Scheme 3). The desired product 6k could be afforded in 96% yield (1.3 g). Some synthetic transformations of the dearomatized products have been examined. The mixture of two diastereoisomers of 5g(1:1 dr) could be decarboxylated to form 7 in 80% yield. The newly formed C-N bond of 6k could be cleaved

Scheme 2 Substrate scope of esters.

Table 5 Substrate scope of amines^a

 a 1a (0.2 mmol), 2 (0.4 mmol), pre-synthesized PdCl₂–BINAP complex (0.01 mmol), Ag₃PO₄ (0.2 mmol), and Na₂HPO₄ ·12H₂O (0.4 mmol) in DMA (1.0 mL) at 120 °C.

Scheme 3 Gram-scale reaction and transformations of the products.

by the hydrogenolysis reaction with Pd/C, leading to 8 in excellent yield. In addition, the β -diketone compound 4a could be condensed with hydroxylamine hydrochloride and hydrazine

monohydrate, furnishing the corresponding isoxazole 9 and pyrazole 10 in good yields, respectively.

Conclusions

In summary, we have developed a Pd-catalyzed dearomative 1,4-difunctionalization of naphthalene derivatives by mimicking the reactivity of simple conjugated dienes in more challenging electronically unbiased aromatic systems. Diverse nucleophiles were found to be compatible with the reaction conditions. Various functionalized spirooxindoles could be obtained efficiently in good to excellent yields (up to 99%) with exclusive diastereoselectivity. Further exploration of the application of this methodology is currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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