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Formal Aromaticity-Transfer for Palladium-Catalyzed Coupling between Phenols and Pyrrolidines/Indolines

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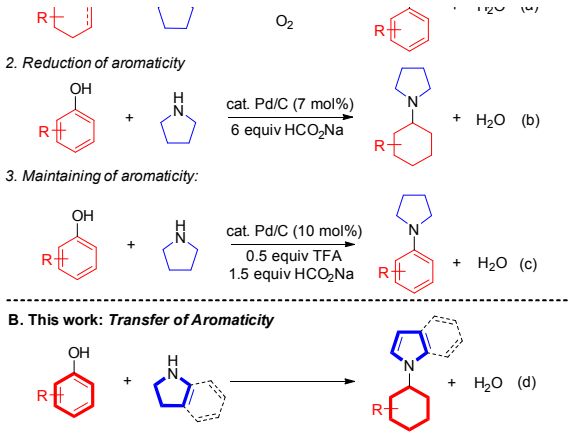
We herein describe a palladium-catalyzed formal aromaticity-transfer coupling reaction between phenols and pyrrolidines or indolines to generate the corresponding *N*-cyclohexyl pyrroles or indoles. In this transformation, the aromaticity of phenols is formally passed on to the pyrrolidines or indolines units. Substituted phenols thus can serve as latent cyclohexyl equivalents for a fast construction of various *N*-cyclohexyl pyrroles and indoles.

Phenols are widely available and can be obtained at low cost from nature, since they comprise one of the basic units in the lignocellulosic biomass as well as coal.[1] Therefore, phenols are ideal aromatic coupling partners and cyclic C-6 feedstocks because of their renewable and sustainable profiles. Past decades have witnessed tremendous progress of the cross-coupling (C-O bond cleavage) of phenol derivatives, pioneered by Shi,[2] Chatani,[3] Martin[4] and others.[5] In addition, phenols can potentially be used as cyclohexyl synthons due to their facile reduction, in which cyclohexanone or cyclohexenone can be obtained under controlled hydrogenation conditions.[6] The combination of their reductive and renewable features led to increasing interests in the selective reduction and transformation of phenols and cyclohexanones or cyclohexenones (the reduced forms of phenols) in recent years.[7]

Previously, we and others developed a homogeneous palladium-catalyzed "oxidative aromatization process" to synthesize aromatic amines utilizing cyclohexanone or cyclohexenone as cyclic-aromatic synthons (Scheme 1, a).[7g, 7l] Recently, a reductive coupling reaction between phenols and amines to form cyclohexylamines was succeeded using phenols as cyclohexyl synthons under Pd/C-catalyzed transfer hydrogenation conditions (Scheme 1, b),[7k] which was also successful in a flow reactor.[8] Later, a formal direct-coupling of phenols with amines to generate aromatic amines was realized via an in situ hydrogenation-dehydrogenation ("H-borrowing") strategy to maintain the aromatic nature of the starting phenol ring overall (Scheme 1, c).[7j] Inspired by these early successes, we are intrigued by the possibility of aromaticity-transfer reaction between phenols and pyrrolidines/indolines to afford the *N*-cyclohexyl pyrroles/indoles (Scheme 1, d). Both atom-economy[9] and redox-economy[10] are highlighted in such transformation since the aromaticity of phenols will be further reinstalled into the pyrrolidine or indoline motifs in this process. Furthermore, the aromaticity-transfer products, *N*-cyclohexyl pyrroles/indoles, are valuable units in various bio-active molecules such as antitumor, antibacterial, and antiviral agents.[11]



Scheme 1. Design of the aromaticity-transfer reaction.

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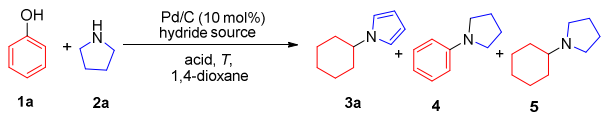
Table 1 Optimization of the reaction conditions[a]

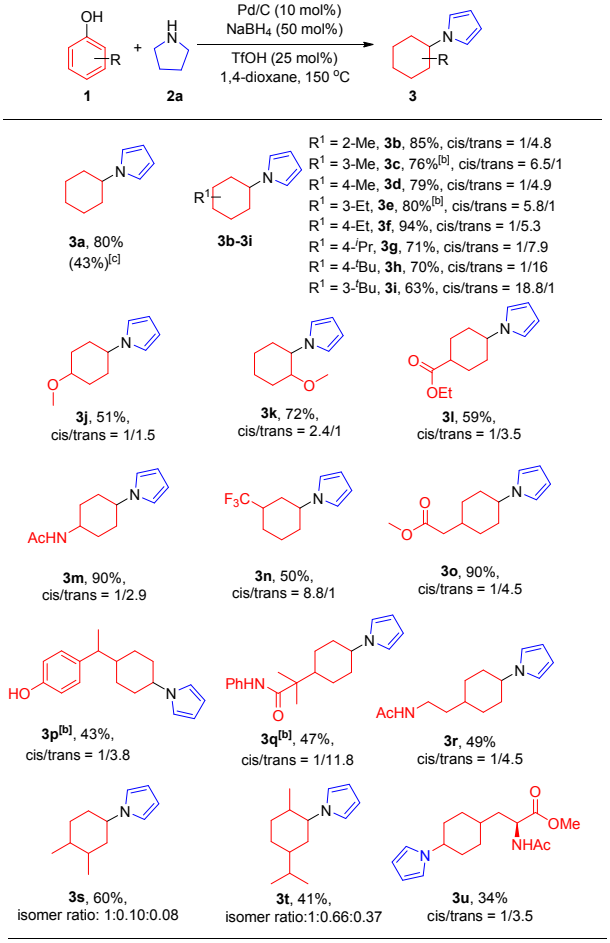


entry	hydride source (mol%)	acid (mol%)	T (°C)	Yield (%) 3a	4	5
1[b]	HCO_2Na (150)	-	140	9	27	32
2	HCO_2Na (150)	-	140	31	41	14
3	HCO_2Na (150)	$PhCO_2H$ (50)	140	23	43	6
4	HCO_2Na (150)	TFA (50)	140	56	20	13
5	HCO_2Na (150)	TfOH (50)	140	69	8	10
6	HCO_2Na (150)	TfOH (50)	160	71	13	2
7	HCO_2Na (200)	TfOH (50)	160	61	20	9
8	HCO_2Na (200)	TfOH (100)	160	77	7	7
9	HCO_2Na (200)	TfOH (100)	150	75	5	11
10	$NaBH_4$ (50)	TfOH (100)	150	40	20	18
11	$NaBH_4$ (50)	TfOH (50)	150	71	5	10
12	**$NaBH_4$ (50)**	**TfOH (25)**	**150**	**80 (80)**	**8**	**4**

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), pyrrolidine (0.28 mmol, 1.4 equiv), 10 mol% of 5 wt% Pd/C, acid with hydride source in 1,4-dixoane (1 mL) were stirred under argon in 10-mL sealed tube for 12 h; NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, with isolated yield given in parentheses; [b] Toluene was used as the solvent. For details of optimization, please see the supporting information (SI); TFA = trifluoroacetic acid; TfOH = trifluoromethanesulfonic acid.

To investigate the feasibility of our hypothesis, we initially tested the reaction of phenol with pyrrolidine by using Pd/C as the catalyst, 1.5 equiv HCO_2Na as the hydride source and toluene as the solvent at 140 °C (Table 1, entry 1). Gratifyingly, the desired aromaticity-transfer product *N*-cyclohexyl pyrrole (**3a**) could be obtained in 9% NMR yield along with the two by-products: the direct cross-coupling product, *N*-phenyl pyrrole (**4**), as well as the net reduction product, *N*-cyclohexylamine (**5**). A strong solvent effect was observed in this transformation. When dioxane was used as the solvent instead of toluene (Table 1, entry 2), the yield of desired product **3a** was significantly increased to 31%. Since acids can promote the condensation of ketone with amine, various acids were evaluated (Table 1, entries 3-5 & see supporting information (SI), Table S1). Generally, Brønsted acids worked better than Lewis acids (Table S1) and among all the Brønsted acids examined, stronger acids gave better results than weaker acids. Following this trend, TfOH showed the best efficiency, generating the desired product in 69% NMR yield (Table 1, entry 5). Elevating the reaction temperature from 140 °C to 160 °C slightly increased the desired product yield (Table1, entry 6). Increasing the amount of HCO_2Na from 1.5 equiv to 2.0 equiv decreased the yield slightly; however, when the amount of TfOH was simultaneously increased from 0.5 equiv to 1.0 equiv, the yield was improved to 77% (Table 1, entries 7-8). This might suggest that a balanced combination of acidity and hydride donor amount was essential in this reaction system. Lowering the temperature from 160 °C to 150 °C showed similar reaction efficiency (Table 1, entries 8-9). When we tried to use the entry 9 conditions to explore the reaction scope initially, unfortunately, we found that the conversion of phenols was low

Table 2 Substrate scope of phenols[a]



[a] Reaction conditions: phenols (0.2 mmol, 1 equiv), pyrrolidine (0.28 mmol, 1.4 equiv), Pd/C (10 mol%), $NaBH_4$ (50 mol%), TfOH (25 mol%) in 1,4-dioxane (1 mL) were stirred at 150 °C under argon in 10-mL sealed tube for 12 h; isolated yields were given unless otherwise noted; cis/trans (isomer) ratio was determined by crude ^{1}H NMR. [b] 62.5% $NaBH_4$ was used. [c] 3-Methoxyphenol was used as substrate and NMR yield was given with 1,3,5-trimethoxybenzene as internal standard.

with phenols bearing bulky substituents, such as 3-*tert*-butyl-phenol. To overcome this problem, $NaBH_4$, which is a stronger hydride donor than HCO_2Na,[12] was used as the hydride source to re-examine the reaction system (Table 1, entries 10-12 & Table S2). Ultimately, by carefully selecting the combination of acid and the amount of $NaBH_4$ (Table S2), the desired product could be obtained in 80% yield (Table 1, entry 12).

With the optimized conditions in hand, the substrate scope of phenols was explored next. As shown in Table 2, various alkyl substituted phenols reacted smoothly to afford the corresponding products in moderate to excellent yields (Table 2, **3b-3i**). Bulky alkyl substituted phenols such as 3 or 4-*tert*-butyl phenols, relatively more difficult to reduce due to their steric hindrance, reacted well to give 63% and 79% yields,

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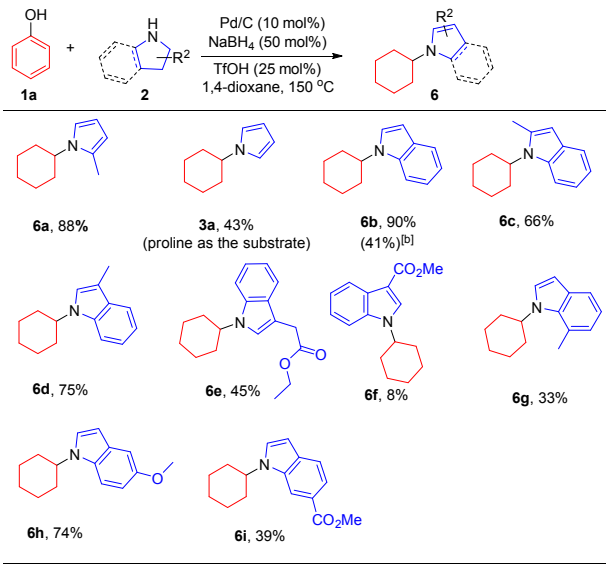
respectively. The cis/trans ratio followed the trend of the steric size of alkyl substituents on phenols. For example, as shown in **3d**, **3f** and **3h**, the cis/trans ratio changed from 1/4.9 to 1/16 with the increase in the substituent size, suggesting a thermodynamically controlled process in which the trans-isomer is more favourable with the increasing size of 4-alkyl substituent in the cyclic six-membered ring conformation.[16] Phenols bearing both electron-withdrawing and electron-donating substituents all worked well to give the corresponding products in moderate to excellent yields, with electron-donating substituent giving a higher yield than electron-withdrawing one (**3m** vs **3l**). As expected, both *ortho*- or *para*- methoxy phenols afforded the desired products smoothly; however, with the *meta*-methoxy phenol, the Ar-OMe bond was completely cleaved during the reaction to give *N*-cyclohexyl pyrrole (**3a**) in 43% yield likely due to the facile *β*-elimination of the 3-methoxycyclohexanone intermediate.[7k] When 4-fluorophenol was used as substrate, the defluorination product was obtained, which was consistent to our previous reports.[7j] It was worth mentioning that the trifluoromethyl (**3n**), an extra phenolic OH (**3p**) and a sterically bulky amide (**3q**) were all tolerated in this transformation. Moreover, bio-active phenol derivatives, such as Tyramine and Tyrosine, were suitable substrates for this transformation (**3r** and **3u**). Besides, di-substituted phenols also reacted efficiently to give the desired products in moderate yields (**3s** and **3t**). Importantly, carvacrol, a natural product from the essential oil of *Origanum vulgare*, underwent this transformation as well (**3t**).

On the other hand, the substrate scope of pyrrolines/indolines was investigated as summarized in Table 3. Indoline worked well to give the corresponding *N*-cyclohexylindole (**6b**) in 90% isolated yield. The alkyl substituted pyrroline or indolines such as 2-methylpyrrolidine and 2- or 3-methylindolines were all effective substrates, affording the corresponding pyrrole and indole derivatives in good to excellent yields (**6a**, **6c**, **6d**), while the 7-methylindoline gave the corresponding product in relatively lower yield probably due to the steric hindrance of 7-Me group (**6g**). Interestingly, when proline or indoline-2-carboxylic acid were used as substrates, the corresponding decarboxylation products were generated in moderate yields;[7l, 13] however, the corresponding methyl esters of proline and indoline-2-carboxylic failed to give the products. The indoline-3-carboxylic methyl ester gave a low yield while indoline-3-ethyl acetate could afford the product in moderate yield (**6f**, **6e**). Indoline with electron-donating substituent worked better than electron-withdrawing one (**6h**, **6i**), in line with the nucleophilicities of the indoline derivatives.

To investigate the possible mechanism, cyclohexanone and cyclohexenone (the two possible reduced forms of phenol) were used (Scheme 2, a and b). Both compounds could afford the desired product in 62% and 47% NMR yields, respectively. To further understand the mechanism, the kinetic profile of this transformation was studied in Figure 1 (see SI for details). The desired product **1a** increased as the reaction proceeded. Interestingly, the two by-products *N*-phenylpyrrolidine (**4**) and *N*-cyclohexylpyrrolidine (**5**) were formed in reasonable amounts at onset of this transformation, decreased to relatively small amount at the end of the reaction. The observation indicated that the two redox-isomers: *N*-phenylpyrroline (**4**) and *N*-cyclohexylpyrrolidine (**5**)

Table 3 Substrate scope of pyrrolidines/indolines[a]



[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), pyrrolidines (0.28 mmol, 1.4 equiv) or indolines (0.48 mmol, 2.4 equiv), Pd/C (10 mol%), TfOH (25 mol%) in 1,4-dioxane (1 mL) were stirred at 150 °C under argon in 10-mL sealed tube for 12 h; isolated yields were given. [b] Indoline-2-carboxylic acid was used as substrate.

could be potentially converted into the desired product *N*-cyclohexylpyrrole (**3a**). To examine this possibility, the control experiments were tested (Scheme 2, c and d). As expected, both **4** and **5** could be converted into **3a** in 48% and 55% NMR yields, respectively.

Based on the above results, a tentative mechanism for this formal aromaticity transfer reaction is proposed in Scheme 3. This reaction could be initiated by the $NaBH_4$ reacted with palladium catalyst to generate the $HPd^{II}H$ species,[7j, 15] which would reduce phenol (**3a**) to form the cyclohexanone or cyclohexenone (**I**). Then, intermediate **I** could undergo fast condensation with pyrroline (**2a**), catalyzed by TfOH, to give the key intermediate **II**. If intermediate **II** went through 1,3-hydride transfer to give intermediate **III**,[14] intermediate **IV** could be generated after deprotonation**.** Next, the desired product (**3a**) could be obtained by dehydrogenation of intermediate **IV** catalyzed by palladium to regenerate the $HPd^{II}H$ species,[7j,15] as stated in **Pathway A**. Alternatively, based on our previous work (Scheme 1, b and c),[7k, 7j] intermediate **II** could also be transformed to intermediates **4** or **5**. Based on the results of control experiments (Scheme 2), intermediates **4** and **5** could both afford the desired product **3a** by either hydrogenation process (**Pathway B**) or dehydrogenation process (**Pathway C**) catalyzed by palladium.

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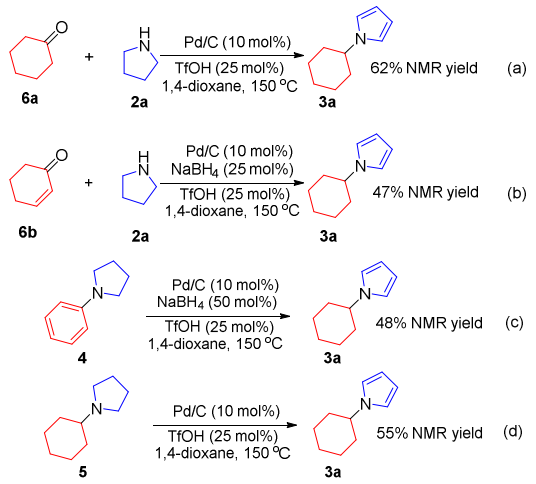
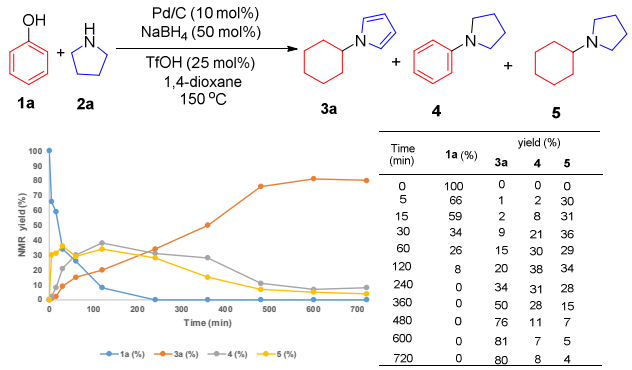
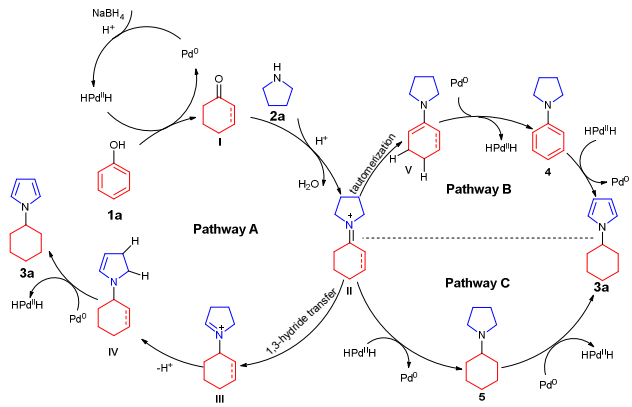


Scheme 2. Control experiments.



Time (min)	1a (%)	yield (%) 3a	4	5
0	100	0	0	0
5	66	1	2	30
15	59	2	8	31
30	34	9	21	36
60	26	15	30	29
120	8	20	38	34
240	0	34	31	28
360	0	50	28	15
480	0	76	11	7
600	0	81	7	5
720	0	80	8	4

Figure 1. Kinetics profile.



Scheme 3. Tentative mechanism.

Conclusions

In conclusion, we have developed a formal aromaticity-transfer reaction between phenols and pyrrolines/indolines, featuring atom- and redox-economies. A wide range of *N*-cyclohexylpyrroles and *N*-cyclohexylindoles bearing various functional groups were obtained by this novel method, starting from the naturally abundant and sustainable phenols. Several bio-active phenols such as Tyramine, Tyrosine and Carvacrol are all suitable substrates in this transformation. Ongoing studies regarding the synthetic applications of such transformations are currently underway in our laboratory.

Acknowledgements

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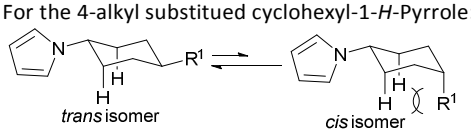
16 For the 4-alkyl substituted cyclohexyl-1-*H*-Pyrrole:



thermodynamically, trans favored over *cis* isomer

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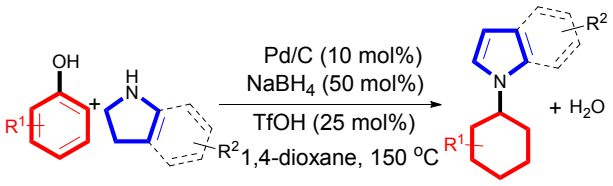

- *Formal aromaticity-transfer*
- *Phenols as cyclohexyl synthons*
- *Redox and atom efficiencies are presented*
- *30 examples up to 94% yield*

A formal “aromaticity-transfer” reaction between phenols and pyrrolines/indolines has been developed: a redox- and atom-efficient method to synthesize N-cyclohexylpyrroles/indoles.