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# Access to *N*-unprotected 2-amide-substituted indoles from Ugi adducts *via* palladium-catalyzed intramolecular cyclization of *o*-iodoanilines bearing furan rings†

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A variety of *N*-unprotected 2-amide-substituted indoles were synthesized from readily available furfural-based Ugi adducts in moderate to good yields *via* palladium-catalyzed intramolecular cyclization of *o*-iodoanilines bearing furan rings. These reactions involved a cascade sequence consisting of dearomatizing arylation, opening of the furan ring, and deprotection of the N atom.

Polyfunctionalized indoles, including 2-amide-substituted indoles, are privileged motifs in medicinal chemistry and synthetic organic chemistry.<sup>1</sup> The indole ring is probably the most common heterocycle found in natural products and pharmaceuticals,<sup>2</sup> and functionalized indoles are versatile building blocks for the preparation of structurally complex and novel indolines, many of which show potent bioactivities (Fig. 1).<sup>3</sup> Thus, much effort has been devoted to the development of strategies for the synthesis and functionalization of indoles and their derivatives.<sup>4</sup> Among them, the most attractive routes are those involving transition-metal-catalyzed intermolecular or intramolecular cyclization of *o*-haloanilines with alkenes,<sup>5</sup> alkynes,<sup>6</sup> or allenes.<sup>7</sup> Despite the attractiveness of these routes, it would be desirable to develop efficient catalytic methods for the preparation of functionalized indoles from *o*-haloanilines and furans, which are readily available, alternatives to alkenes for diversity-oriented synthesis strategies.<sup>8,9</sup>

We speculated that Ugi adducts might be useful for this purpose. Ugi reactions involve four components—an aldehyde or ketone, an isocyanide, an amine, and a carboxylic acid—and afford a diverse array of functionalized  $\alpha$ -acylamino amides,<sup>10</sup> which can be subjected to a wide variety of post-condensation transformations to achieve further structural diversity.<sup>11</sup> Recently, we and other groups developed a route to functionalized indoles *via* palladium-catalyzed intramolecular arylative dearomatization of 2-bromo-*N*-(furan-2-ylmethyl)anilines.<sup>3f,12</sup> In this paper, we report a convenient protocol for the synthesis of  $\alpha$ -amide-substituted indoles *via* palladium-

catalyzed intramolecular arylative cyclization of furans that were generated by Ugi reactions of furfurals and *o*-haloanilines (Scheme 1).

The success of this protocol relies on suppression of the following side reactions:  $\beta$ -arylation of the furan ring, protonation of the ArI, and intramolecular C–N coupling. With this in mind, we chose *N*-(*tert*-butyl)-2-(furan-2-yl)-2-(*N*-(2-iodophenyl)acetamido)acetamide (**1a**)—which was prepared by means of a Ugi reaction of furfural, 2-iodoaniline, acetic acid, and *tert*-butyl isocyanide—as the substrate for optimization of the reaction conditions. We were pleased to find that upon treatment of **1a** with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 equiv.), PPh<sub>3</sub> (0.1 equiv.), and K<sub>2</sub>CO<sub>3</sub> (2 equiv.) in 1,4-dioxane at 70 °C for 12 h, polysubstituted *N*-unprotected indole **2a** was obtained in 30% yield along with unidentified by-products (Table 1, entry 1). This transformation clearly involved a cascade sequence consisting of arylation, ring-opening, and *N*-deacetylation. The *in situ* *N*-deacetylation is particularly interesting and useful and may have resulted from the weaker nucleophilicity of the N atom of the indole ring

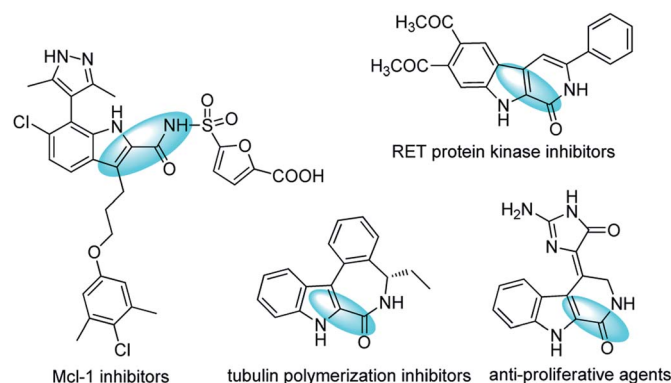


Fig. 1 Bioactive 2-amide-substituted indoles.

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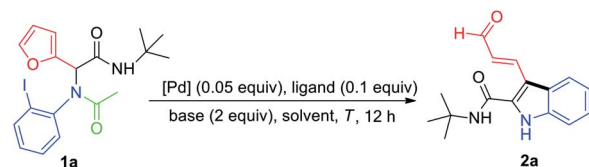
relative to that of the amide N of **1a**. Other bases ( $\text{Cs}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) were also tested, but **2a** was not detected in any of these reactions (entries 2–5). Stronger base of  $\text{Cs}_2\text{CO}_3$  resulted in side-reaction of C–N coupling.  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  as the base mostly led to the protonated product. DBU led to no reaction. Next, we attempted to improve the yield of **2a** by increasing the reaction temperature (entries 6–9), and an 89% yield was obtained at 110 °C. Screening of various ligands other than  $\text{PPh}_3$  failed to produce better results (entries 10–13), and  $\text{Pd}(\text{PPh}_3)_4$  was the optimal catalyst (compare entry 2 with entries 14–17). Evaluation of other solvents (THF, toluene, and DMSO) did not improve the yield (entries 18–20). Therefore, we concluded that the optimal conditions involved the use of  $\text{Pd}(\text{PPh}_3)_4$  (0.05 equiv.) as the catalyst,  $\text{K}_2\text{CO}_3$  (2.0 equiv.) as the base, 1,4-dioxane as the solvent, and 110 °C as the reaction temperature.

With the optimized conditions in hand, we prepared a series of Ugi adducts **1** with various  $\text{R}^1$ – $\text{R}^4$  groups and a furan moiety in moderate yields, and we subjected the resulting compounds to the arylytic cyclization conditions to investigate the substrate scope (Table 2). In all cases, the reaction proceeded smoothly to afford corresponding indoles **2** in moderate to good isolated yields (40–77%). Specifically, with  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{Me}$ , and  $\text{R}^4 = t\text{-Bu}$ , several  $\text{R}^3$  groups (H, Me,

F, and Cl) were screened and found to provide corresponding indolyl aldehydes **2a–2d** in 45–66% yields (entries 1–4). Reaction of **1c**, which bears an electron-withdrawing 4-F group, gave a substantial amount of a by-product generated by protonation without opening of the furan ring, which resulted in a relatively low yield of **2c** (45%). Similarly, with  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Me}$ , and  $\text{R}^4 = t\text{-Bu}$ , compounds with H, Me, MeO, and  $\text{CF}_3$  at  $\text{R}^3$  afforded **2e–2h** in 60–77% yields (entries 5–8). Substrate **1h**, which has an electron-withdrawing 4- $\text{CF}_3$  at  $\text{R}^3$ , gave a lower yield (60%) than the other three substrates. In addition to H or Me,  $\text{R}^1$  could be Ph or 4-Me-Ph: **2i** and **2j** were obtained in 67% and 72% yields, respectively (entries 9 and 10). Notably, when  $\text{R}^2$  was an aryl group (4-MeO-Ph), **2e** was produced in 77% yield (entry 11). In contrast, when  $\text{R}^3$  was *n*-Pr, the yield of **2e** was only 40% (entry 12). Finally, when  $\text{R}^4$  was cyclohexyl, **2m–2o** were obtained in good yields (entries 13–15).

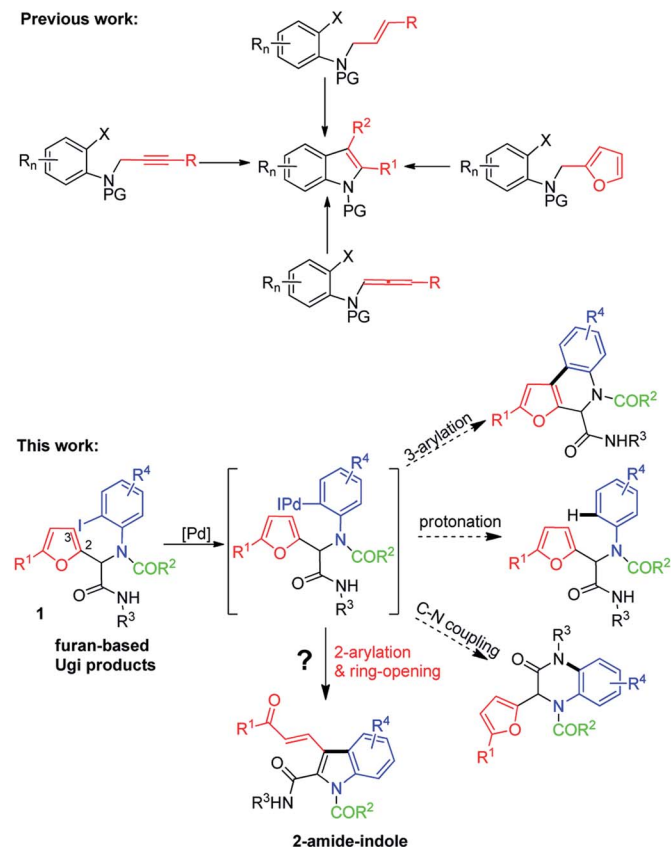
Products **2** bear amide, carbonyl and alkenyl functional groups, all of which are amenable to numerous further

Table 1 Optimization of reaction conditions<sup>a</sup>



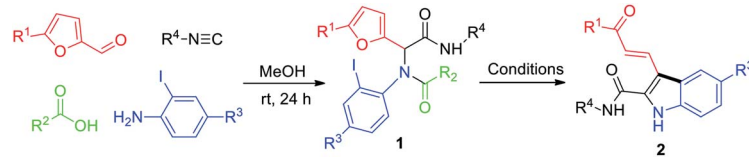
Entry	[Pd]	Ligand	Base	T (°C)	Yield <sup>b</sup> (%)
1	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	70	30
2	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{Cs}_2\text{CO}_3$	70	ND
3	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{NaHCO}_3$	70	ND
4	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{Na}_2\text{CO}_3$	70	ND
5	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	DBU	70	ND
6	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	80	31
7	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	100	44
8	<b><math>\text{Pd}(\text{PPh}_3)_4</math></b>	<b><math>\text{PPh}_3</math></b>	<b><math>\text{K}_2\text{CO}_3</math></b>	<b>110</b>	<b>89</b>
9	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	120	25
10	$\text{Pd}(\text{PPh}_3)_4$	DPPP	$\text{K}_2\text{CO}_3$	110	18
11	$\text{Pd}(\text{PPh}_3)_4$	DPPB	$\text{K}_2\text{CO}_3$	110	19
12	$\text{Pd}(\text{PPh}_3)_4$	DPPF	$\text{K}_2\text{CO}_3$	110	12
13	$\text{Pd}(\text{PPh}_3)_4$	Xantphos	$\text{K}_2\text{CO}_3$	110	48
14	$\text{Pd}_2(\text{dba})_3$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	50
15	$\text{Pd}(\text{OAc})_2$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	18
16	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	54
17	$\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	31
18 <sup>c</sup>	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	45
19 <sup>d</sup>	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	21
20 <sup>e</sup>	$\text{Pd}(\text{PPh}_3)_4$	$\text{PPh}_3$	$\text{K}_2\text{CO}_3$	110	66

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), catalyst (0.05 equiv.), ligand (0.1 equiv.), and base (2 equiv.) in 2.0 mL of 1,4-dioxane were allowed to react under nitrogen for 12 h. DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DPPP, 1,3-bis(diphenylphosphino)propane; DPPB, 1,4-bis(diphenylphosphino)butane; DPPF, 1,1'-bis(diphenylphosphino)ferrocene; xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene. <sup>b</sup> Yields were determined by <sup>1</sup>H NMR spectroscopy. ND = not detected. <sup>c</sup> THF was the solvent. <sup>d</sup> Toluene was the solvent. <sup>e</sup> DMSO was the solvent.



Scheme 1 Pd-catalyzed approaches to polyfunctionalized indoles from *o*-haloanilines.



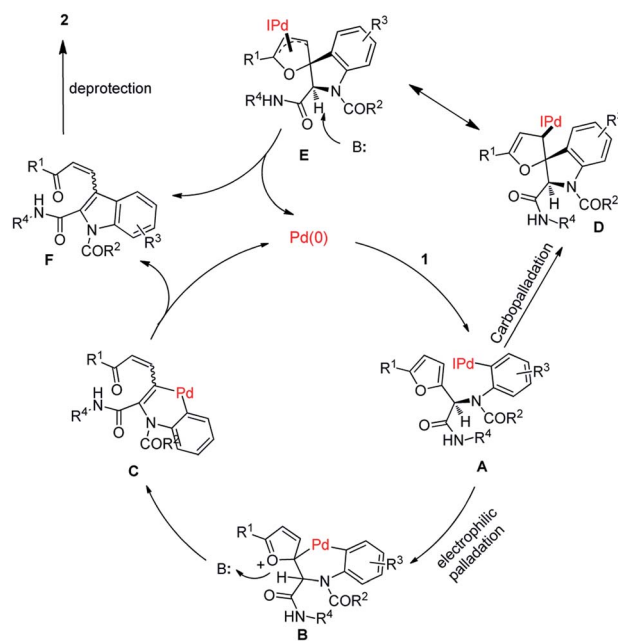
Table 2 Substrate scope<sup>a</sup>


Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	1 (% yield <sup>b</sup> )	2 (% yield <sup>b</sup> )
1	H	Me	H	<i>t</i> -Bu	<b>1a</b> (50)	<b>2a</b> (66)
2	H	Me	Me	<i>t</i> -Bu	<b>1b</b> (45)	<b>2b</b> (63)
3	H	Me	F	<i>t</i> -Bu	<b>1c</b> (52)	<b>2c</b> (45)
4	H	Me	Cl	<i>t</i> -Bu	<b>1d</b> (41)	<b>2d</b> (64)
5	Me	Me	H	<i>t</i> -Bu	<b>1e</b> (42)	<b>2e</b> (77)
6	Me	Me	Me	<i>t</i> -Bu	<b>1f</b> (42)	<b>2f</b> (63)
7	Me	Me	MeO	<i>t</i> -Bu	<b>1g</b> (40)	<b>2g</b> (70)
8	Me	Me	CF <sub>3</sub>	<i>t</i> -Bu	<b>1h</b> (40)	<b>2h</b> (60)
9	Ph	Me	H	<i>t</i> -Bu	<b>1i</b> (46)	<b>2i</b> (67)
10	<i>p</i> -Tolyl	Me	H	<i>t</i> -Bu	<b>1j</b> (33)	<b>2j</b> (72)
11	Me	PMB	H	<i>t</i> -Bu	<b>1k</b> (55)	<b>2e</b> (77)
12	Me	<i>n</i> -Pr	H	<i>t</i> -Bu	<b>1l</b> (32)	<b>2e</b> (40)
13	Me	Me	H	Cy	<b>1m</b> (57)	<b>2m</b> (50)
14	Me	Me	MeO	Cy	<b>1n</b> (53)	<b>2n</b> (61)
15	Me	Me	CF <sub>3</sub>	Cy	<b>1o</b> (42)	<b>2o</b> (66)

<sup>a</sup> Reaction conditions: **1** (0.2 mmol), catalyst (0.05 equiv.), ligand (0.1 equiv.), and base in 2.0 mL solvent were allowed to react at 110 °C for 12 h. Cy, cyclohexyl. <sup>b</sup> Isolated yields are given.

transformations that can be used to prepare structurally diverse indoles. For example, hydrogenation of the double bonds of **2e–2g** and **2i** afforded the corresponding products (**3e–3g** and **3i**) in good yields (Scheme 2).

In Scheme 3, we depict two possible pathways for this transformation (electrophilic palladation and carbopalladation) on the basis of the above-described experimental results and previously reported results regarding arylation of furans.<sup>12,13</sup> Specifically, an oxidative addition reaction between aryl iodide **1** and palladium(0) forms intermediate **A**. Intramolecular electrophilic palladation of the furan ring of **A** at the  $\alpha$ -position results in the generation of intermediate **B**, which undergoes base-mediated furan ring-opening and  $\beta$ -elimination to afford intermediate **C**. A reductive elimination reaction of **C** provides **F** and palladium(0), completing the catalytic cycle. Deprotection of **F** yields **2**. Alternatively, **A** undergoes carbopalladation to form intermediate **D**, which isomerizes to  $\pi$ -allylic palladium complex **E**. Ring-opening of **E** produces **F**.

Scheme 3 Possible pathway for the formation of **2**.Scheme 2 Hydrogenation of **2**.

## Conclusions

In summary, we have developed a protocol for the synthesis of *N*-unprotected 2-amide-substituted indoles by means of Pd-



catalyzed dearomatizing intramolecular arylation reactions of readily available furfural-based Ugi adducts. This protocol involves an intramolecular condensation of an *o*-haloaniline bearing a furan ring and a subsequent cascade involving dearomatizing arylation, opening of the furan ring, and *N*-deprotection. The bioactivities of the obtained polysubstituted indoles are being explored in our laboratory, and the results will be reported in due course.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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