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Synthesis of highly substituted dibenzoazocine derivatives by the aza-Claisen rearrangement and intramolecular Heck reaction via 8-*exo*-trig mode of cyclization

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ABSTRACT

The synthesis of highly substituted dibenzo-azocine systems is still lacking. An efficient synthetic protocol utilizing the sequential aromatic aza-Claisen rearrangement followed by the implementation of the intramolecular Heck reaction as a key step has been developed for the synthesis of various dibenzo-azocine derivatives of biological relevance.

Medium-sized nitrogen heterocycles, especially eight-membered azocines, are key intermediates occurring in many natural products.[1,2] Besides, medium-sized heterocycles fused to aryl rings are found in many drugs and preclinical leads. An important scaffold is the dibenzo[*b*,*f*]azocine present in psychotropic drugs such as Imipramine, Desipramine and Bonnecore.[3] Despite their biological activity, azocine fused systems are not sufficiently investigated, one possible barrier to this generally being unsatisfactory synthetic procedures.[4]

Modern organic synthesis emphasizes the utilization of reactions that require a minimal amount of labour and allow for the construction of complex molecules in a time and cost effective manner. During the past decade, major efforts have been devoted to the development of palladium-mediated organic reactions, which, by virtue of their ease of compatibility, complexity and diversity, may bring about potential and highly effective transformation.[5] Recently, the search of more novel methods for the construction of organic molecules from simple starting materials has been an ongoing challenge. In general, not many methods are available for the synthesis of medium-sized heterocycles. Among the various synthetic protocols, the palladium-catalyzed intramolecular Heck reaction has become a useful technique due to its excellent functional group tolerance and high stereoselectivity. Recently, we have reported[6] the synthesis of some interesting regular to medium-ring oxa- and oxathia- heterocycles by the application of the intramolecular Heck reaction. However, other groups[7] have also reported the formation of medium-sized heterocyclization by palladium-catalyzed Heck reactions, but none has started with the unactivated allylic C–H activation method. Moreover, though the formation of medium-sized oxa-heterocycles is relatively abundant,[6,8] medium-sized nitrogen heterocycles by the implementation of intramolecular Heck reactions are rare and still significant from the synthetic point of view. It is reported[9] that palladium-catalyzed cyclization by the application of intramolecular Heck reactions require harsh reaction conditions where a nitrogen-containing compound is used as the starting material. Recently, Guy et al[10] have presented eight-membered azocines by the intramolecular Heck reaction via the 8-*endo-trig* mode of cyclization starting from highly activated precursors. Therefore, all the findings prompted us to undertake the synthesis of biologically interesting azocine intermediates by the application of the palladium-mediated intramolecular Heck reaction via the 8-*exo-trig* mode of cyclization starting from unactivated allylic systems.

The aza-Claisen rearrangement of *N*-allylaniline under thermal conditions requires drastic conditions[11] compared to the corresponding oxy-Claisen rearrangement. However, such rearrangement generally occurs with a significant amount of rate enhancement under catalyzed conditions.[11,12] Moreover, it has been found that the presence of an additional[13] alkyl group in the *N*-alkylaniline greatly increases the rate of the aromatic aza-Claisen rearrangement. Usually, it is a tough job to accomplish the aromatic aza-Claisen rearrangement without using an additional alkyl group in the *N*-allyl moiety and this is due to the fact

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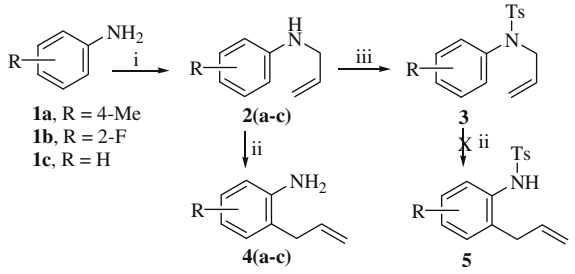
that under catalyzed conditions the rearranged C-allyl product immediately cyclizes to give the corresponding indoline[14] derivatives. Besides, a number of unidentified side products are also formed. Therefore, this led us to explore a selective monorearrangement products of *N*-allylaniline derivatives as a possible route for the preparation of our desired Heck precursors for the ultimate preparation of the corresponding dibenzo-azocine derivatives.

Accordingly, we prepared *N*-allylaniline **2a** from the reaction of 4-methylaniline **1a** and allyl bromide in refluxing DMF in the presence of anhydrous potassium carbonate (Scheme 1).

The desired aza-Claisen rearrangement of **2a** was effectively accomplished in xylene in the presence of $BF_3{\cdot}Et_2O$ at 140 °C in a sealed tube within a reasonably short period of time (7–8 h) to deliver the corresponding rearrangement product **4a** as the sole product. We have attempted various other conditions to optimize the reaction using other high boiling solvents, changing the catalyst employed including changing the nature of the catalyst, and increasing the reaction time. Instead of improvement of the results, some side products were obtained at the expense of the desired aza-Claisen rearrangement product. Likewise, the aromatic aza-Claisen rearrangement of other substrates were tested by varying the substituent present in the aromatic ring under developed conditions, and the outcome is depicted in Table 1. Here, it is important to note that we have also conducted the aza-Claisen rearrangement using the –Ts substrates **3a**, but we obtained a complicated reaction mixture instead of the desired product.

To this end, the Heck precursor **7** was synthesized by the reaction of *C*-allylaniline **4a** and 2-bromobenzylbromide **6a** in refluxing acetone in the presence of anhydrous K_2CO_3 and a small amount of sodium iodide[15] (Finkelstein condition). When the Heck reaction was carried out with the substrate **7** in the presence of $Pd(OAc)_2$ as catalyst, tetrabutylammonium bromide (TBAB) as additive and

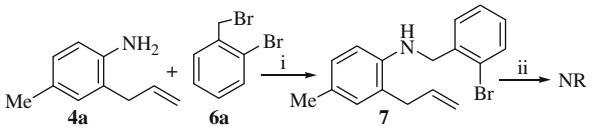


Scheme 1. Reagents and conditions: (i) allyl bromide, DMF, K_2CO_3, reflux, 8 h. (ii) see optimization table 1. (iii) pyridine, TsCl, heat, 4 h.

Table 1
Screening of experimental conditions of the aza-Claisen rearrangement

Entry	Substrate[a]	Catalyst	Solvent	Time (h)	Yield[b] (%)
1	**1a**	1 equiv $BF_3{\cdot}Et_2O$	Xylene	12	55
2[c]	**1a**	**2 equiv $BF_3{\cdot}Et_2O$**	**Xylene**	**7**	**65**
3	**1a**	4 equiv $BF_3{\cdot}Et_2O$	Xylene	7	~60
4	**1a**	2 equiv $BF_3{\cdot}Et_2O$	*o*-DCB	10	~52
5	**1a**	2 equiv $BF_3{\cdot}Et_2O$	Toluene	12	~45
6	**1a**	2 equiv $ZnCl_2$	Xylene	12	CM[d]
7	**1a**	2 equiv AlCl3	Xylene	12	CM[d]
8	**1b**	2 equiv $BF_3{\cdot}Et_2O$	Xylene	8	48
9	**1c**	2 equiv $BF_3{\cdot}Et_2O$	Xylene	7	68
10	**3a**	2 equiv $BF_3{\cdot}Et_2O$	Xylene	7	CM[d]

[a] All reactions were carried out with 1.2 g substrate in 4 ml solvent at 140 °C in a sealed tube.
[b] Isolated yield.
[c] Optimized reaction conditions.
[d] CM = complex reaction mixture.



Scheme 2. Reagents and conditions: (i) acetone, K_2CO_3, NaI, 3.5 h, reflux. (ii) $Pd(OAc)_2$, TBAB, KOAc, DMF, 90 °C, 10–20 h.

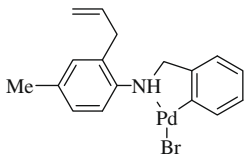
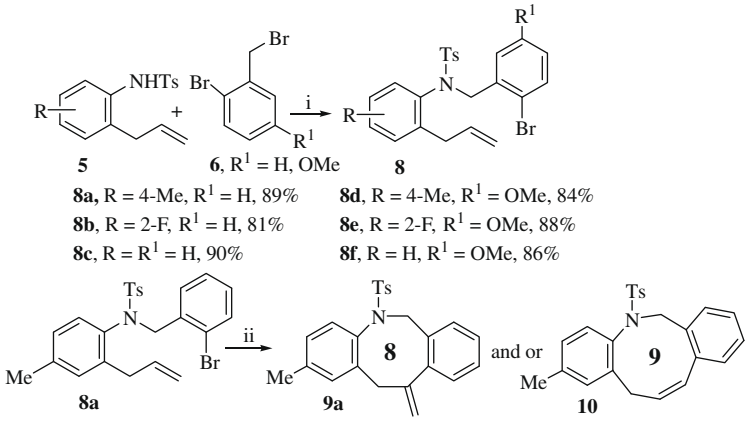


Figure 1.

fused KOAc as base in DMF under a nitrogen atmosphere at 90 °C, for 10–20 h, there was no indication for the formation of the Heck reaction product. The starting material remained unchanged (Scheme 2).

No further improvement was observed even by increasing the reaction temperature. Therefore, we failed to carry out the Heck reaction starting with the substrate **7**. The reason for the failure may be due to the fact that the catalyst $Pd(OAc)_2$ loses its catalytic activity[16] by the formation of the following type of complex (Fig. 1).[17] This may be possible through palladium expanding its



Scheme 3. Reagents and conditions: (i) acetone, K_2CO_3, NaI, 3.5 h, reflux. (ii) $Pd(OAc)_2$, TBAB, KOAc, DMF, N_2 atms, 90 °C, 6 h.

Table 2
Optimization of the Heck reaction.[a]

Entries	Catalyst	Solvent	Base	Yields[c] (%)
1[b]	$Pd(OAc)_2$	DMF	KOAc	72
2	$Pd(OAc)_2$	DMA	KOAc	70
3	$Pd(OAc)_2$	DMF	NaOAc	66
4	$Pd(PPh_3)_2Cl_2$	DMF	KOAc	54
5	$PdCl_2$	DMF	KOAc	NR[d]
6	$Pd(OAc)_2$	Toluene	KOAc	NR[d]
7	$Pd(OAc)_2$	Et_3N	KOAc	NR[d]
8	$Pd(OAc)_2$	THF	KOAc	25
9	$Pd(OAc)_2$	Dioxane	KOAc	NR[d]
10	$Pd(OAc)_2$	CH_3CN	Et_3 N	20
11	$Pd(OAc)_2$	DMF	Ag_2CO_3	NR[d]
12	$Pd(OAc)_2$	DMF	K_2CO_3	NR[d]

[a] All reactions were carried out using TBAB.
[b] Optimized reaction condition.
[c] Isolated yield.
[d] No reaction

valence shell to accommodate the lone pair of electrons of the free NH moiety of the substrate.

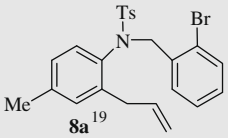
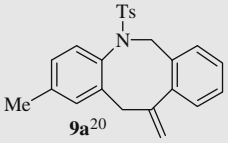
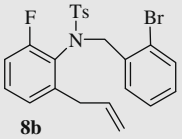
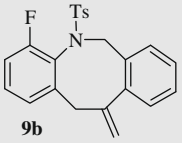
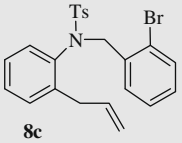
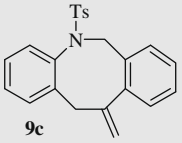
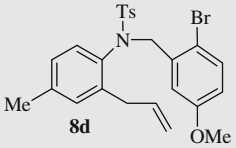
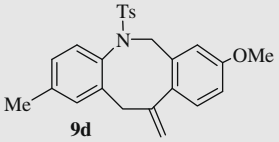
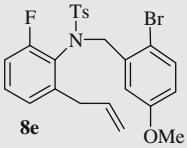
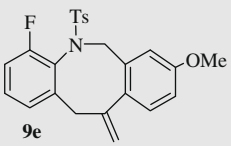
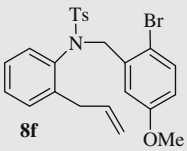
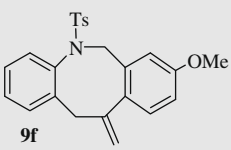
In order to circumvent the possible Pd–N complex, we decided to protect the NH moiety. All the *C*-allylaniline derivatives **4**(**a–c**) were tosylated under the conditions used in scheme 1 to give Heck precursors **8a–f**. The precursors **5** were benzylated with **6** in refluxing acetone–K_2CO_3 in the presence of a small amount of NaI (Finkelstein condition).[15] The intramolecular Heck reaction was conducted with substrate **8a**[19] by applying the concept of Jeffery's two-phase protocol in the presence of $Pd(OAc)_2$, KOAc and tetrabutylammonium bromide (TBAB) in dry DMF under a nitrogen atmosphere for 6 h. The eight-membered *exo*-Heck product (**9a**)[20] was obtained in 72% yield without any contamination of the *endo*-Heck product **10** (Scheme 3).

The resulting *exo*-Heck product was easily characterized from its ^{1}H NMR spectrum, ^{13}C NMR spectrum, HRMS and other analytical data. During the course of optimization of the *exo*-Heck reaction, we observed that the catalyst, base, solvent, additive and temperature also have profound effects on the reaction yield. The optimized results for the synthesis of **9a** are presented in Table 2.

From Table 2, it is seen that though the catalyst $Pd(OAc)_2$ is effective, $PdCl_2$ is totally ineffective for the reaction in DMF. Among the various catalysts used in this reaction to produce the dibenzoazocine derivative, $Pd(OAc)_2$ gave the best results. The reaction afforded no desired product under the reaction conditions described in Table 2 (entries 5–7, 9, 11, and 12). All the reactions were performed in the presence of TBAB as additive, since without TBAB no cyclized product was obtained.

The effect of bases on the reaction was also examined. Conducting the reaction in the presence of organic bases such as Et_3 N

Table 3
Synthesis of dibenzo-azocines by Heck reaction[a]

Entries	Starting	Products	Time (h)	Yields[b] (%)
1	 **8a**[19]	 **9a**[20]	6	72
2	 **8b**	 **9b**	8	73
3	 **8c**	 **9c**	6	75
4	 **8d**	 **9d**	7	79
5	 **8e**	 **9e**	9	73
6	 **8f**	 **9f**	7.5	79

[a] All the reactions were carried out under optimized conditions.
[b] Isolated yield.

changes the outcome of the reaction and only 20% of **9a** was obtained. Replacement of KOAc with NaOAc was also found to be effective (entry 3). The effects of other bases were also studied, and the use of Ag_2CO_3 was found to be ineffective.

A study of the solvent effect (DMF, MeCN, 1,4-dioxane, THF, toluene, Et_3N) suggested that DMF is the best choice. After achieving the optimized results, other substrates **8b–f** were similarly treated under optimized reaction conditions to afford the corresponding *exo*-Heck cyclized products dibenzo-azocines derivatives **9b–f** in 72–79% yields. The results are summarized in Table 3.

The formation of medium-sized *exo*-, and *endo*-Heck products is quite difficult. The formation of the *exo*-Heck product is favoured because of the less steric as well as transannular interaction.[18] The dibenzoazocines were obtained through a 8-*exo*-trig mode of cyclization.

In conclusion, we have developed an efficient synthetic strategy for the selective aromatic aza-Claisen rearrangement of free NH-allylated aniline derivatives for the preparation of *N*-tethered Heck precursors possessing diversity relevant to drug design and drug discovery. The protocol is simple, straightforward and interesting. A synthetic route for the construction of the dibenzoazocine from unactivated allylic substrates by the intramolecular Heck reaction has been developed.

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19. *Some selected spectral data*: Synthesis of Heck precursors **8a**: A mixture of the compounds **5a** (210 mg, 0.697 mmol) and 2-bromobenzylbromide **6a** (191.9 mg, 0.767 mmol) and dry K_2CO_3 (1.0 gm) in dry acetone (50 ml) in the presence of sodium iodide was refluxed for 3.5 h. The reaction mixture was cooled and filtered, and the solvent was removed. The residual mass was extracted with chloroform (3 × 30 ml), washed with water followed by brine-water and dried (Na_2SO_4). Removal of chloroform gave a crude product, which was chromatographed over silica gel (60–120 mesh). Elution of the column with pet. ether–ethyl acetate (5%) gave compounds **8a**.*Compound* **8a**: Yield 89%.; solid; mp 79–80 °C.IR (KBr, cm^{-1}): 1149, 1338, 2852, 2911.^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 2.24 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.18 (d, 2H, J = 6.6 Hz, =CH–CH_2), 4.48 (d, 1H, J = 13.7 Hz, N–CH_aH_b), 4.89 (dd, 1H, J = 11.2 Hz, J = 3.0 Hz, =CH_aH_b), 4.93 (dd, 1H, J = 17.2 Hz, J = 3.0 Hz, =CH_aH_b), 5.09 (d, 1H, J = 13.7 Hz, N–CH_aH_b), 5.36–5.46 (m, 1H, =CH), 6.58 (d, 1H, J = 8.1 Hz, ArH), 6.82 (d, 1H, J = 8.1 Hz, ArH), 6.91 (s, 1H, ArH), 7.04 (t, 1H, J = 7.6 Hz, ArH), 7.17 (t, 1H, J = 7.6 Hz, ArH), 7.30 (d, 2H, J = 7.9 Hz, ArH), 7.39 (d, 2H, J = 7.8 Hz, ArH), 7.60 (d, 2H, J = 7.9 Hz, ArH).^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.1, 21.6, 34.8, 55.1, 116.1, 124.4, 127.1, 127.3, 128.0, 128.1, 129.3, 129.5, 130.7, 131.9, 132.7, 134.2, 134.9, 135.5, 136.8, 138.2, 141.2, 143.6.HRMS: Calculated for $C_{24}H_{24}BrNO_2S$: 492.0609 (M^+), 494.0609 (M+2). Found: 492.0609 (M^+), 494.0591 (M+2).Anal. Calcd for $C_{24}H_{24}BrNO_2S$: C, 61.28; H, 5.14; N, 2.98. Found: C, 61.58; H, 4.89; N, 3.11.
20. General procedure for the synthesis of the compounds **9** by Heck reaction: A mixture of **8a** (100 mg, 0.212 mmol), tetrabutylammonium bromide (82.41 mg, 0.255 mmol) and dry potassium acetate (52.12 mg, 0.531 mmol) was taken in dry *N*,*N*-dimethylformamide (DMF) (10 mL) under nitrogen atmosphere. $Pd(OAc)_2$ (10 mol %, 4.76 mg) was added, and the reaction mixture was stirred at 90 °C for 6 h. The reaction mixture was cooled, water (20 mL) was added, extracted with ethyl acetate (3 × 30 mL) and the ethyl acetate extract was washed with water (2 × 40 mL), followed by brine (30 mL). The organic layer was dried (Na_2SO_4), and the solvent was distilled off to furnish a viscous mass, which was purified by column chromatography over silica gel. Elution of the column with 4% ethyl acetate-petroleum ether afforded the product **9a**.
Compound **9a**: Yield 72%; solid; mp 138–139 °C. IR (KBr, cm^{-1}): 1147, 1330.^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 2.18 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.20 (s, 2H, CH_2), 4.97 (br s, 1H, N–CH_aH_b), 4.99 (br s, 1H, N-CH_aH_b), 5.00 (d, 1H, J = 1.1 Hz, =CH_aH_b), 5.13 (d, 1H, J = 1.1 Hz, =CH_aH_b), 6.74–6.78 (m, 2H, ArH), 6.83 (s, 1H, ArH), 7.01 (d, 2H, J = 6.9 Hz, ArH), 7.10–7.16 (m, 3H, ArH), 7.32–7.35 (m, 1H, ArH), 7.38-7.45 (m, 2H, ArH).
^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 20.9, 21.5, 54.9, 126.3, 126.6, 127.2, 127.3, 127.5, 127.8, 127.9, 128.1, 128.6, 128.8, 128.9, 129.2, 129.5, 130.2, 130.5, 130.9, 131.8, 132.4, 138.1, 143.2, 147.8.
HRMS: Calculated for $C_{24}H_{23}NO_2S$: 412.1347 ($M+Na)^+$. Found: 412.1347 ($M+Na)^+$.
Anal. Calcd for $C_{24}H_{23}NO_2S$: C, 74.00; H, 5.95; N, 3.60. Found: C, 74.19; H, 5.77; N, 3.71.