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ARTICLE TYPE

Synthesis of Allylated Quinolines/Isoquinolines via Palladium-Catalyzed Cyclization-Allylation of Azides and Allyl Methyl Carbonate

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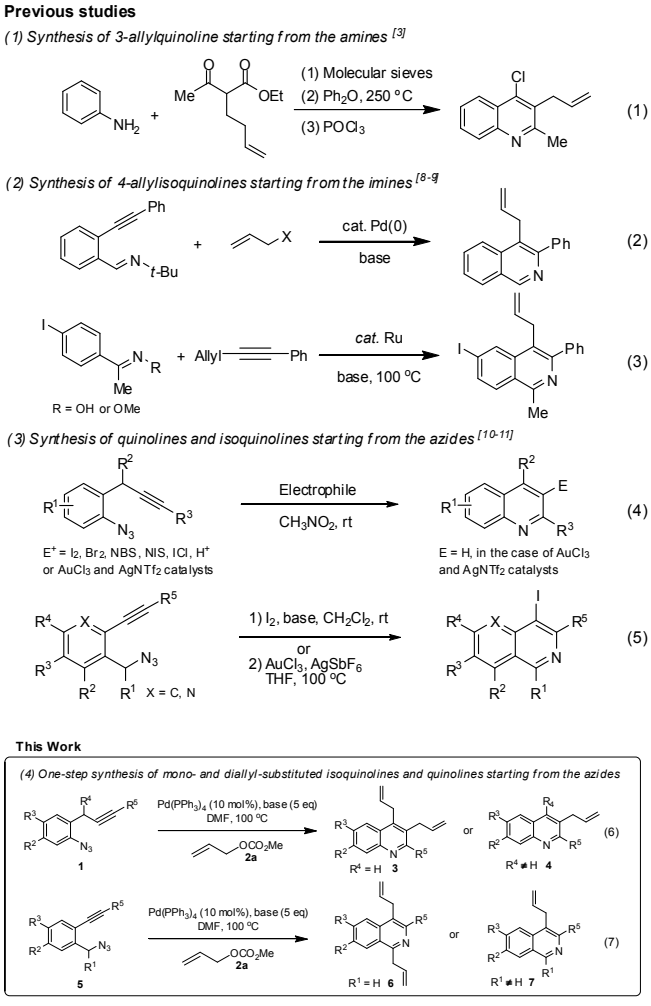
A novel and efficient strategy for the one-step synthesis of allylated quinolines and isoquinolines via palladium-catalyzed cyclization-allylation of azides and allyl methyl carbonate is first developed. The results indicated that the regioselective synthesis of allyl- and diallyl-substituted quinolines/isoquinolines depends on the different substituted groups at R^1 and R^4 positions, such as H or other groups. The reactions proceed smoothly in the presence of $Pd(PPh_3)_4$ and K_3PO_4 or NaOAc in DMF at 100 °C to give the corresponding allyl- and diallyl-substituted quinolines and isoquinolines in good to high yields.

Introduction

Isoquinolines and quinolines are two important classes of heterocyclic compounds because of their wide utility. Substituted isoquinolines and quinolines are often found as structural framework in many biologically active natural products and pharmaceuticals, their physical properties make them beneficial as functional materials [1]. Furthermore, substituted isoquinolines and quinolines can also be used as organocatalysts and meaningful tools for the syntheses of chiral molecules with high enantioselectivity [2]. In particular, allyl-substituted quinolines/ isoquionlines are of special interest because the allyl group sometimes plays an important role in the compound's bioactivity[3]. Besides that, the presence of allyl group makes further cyclization feasible [4].

Owing to their potential usefulness, the synthetic methods for quinoline/isoquinoline derivatives have been extensively studied since its discovery by Gerhardt in 1842 [5-6]. Currently, one of the frequently used methods for allyl-substituted quinolines/ isoquinolines is the coupling between halogen-containing quinolines/isoquinolines and allylic substrates over metal-catalysts [7]. However, a severe drawback of the substitution is that the reaction only works with halogen-containing quinolines/isoquinolines. Thus, its application is limited. Recently, several new synthetic methods for the synthesis of allyl-substituted quinolines/isoquionlines were developed as shown in Scheme 1. Tempone *et al.* [3] reported a two-step process for the synthesis of 3-allylquinolines from the amine and allyl substrates in 2005 (Eq. 1). Larock *et al.* [8] reported an efficient and practical method for the synthesis of 4-allylisoquinolines using *o*-(1-Alkynyl)benzaldimines and allyl halides as starting materials and gave moderate yield (Eq. 2). More recently, Jeganmohan *et al.* [9] reported the intermolecular synthesis of 4-allylisoquinolines from the imines in the presence of $RuCl_2(p$-cymene$)_2$ and gave 55% yield (Eq. 3). Although significant progress has been made in the synthesis of allyl-substituted



Scheme 1 Background and New Reactions

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quinolines/isoquionlines, the reactions hitherto developed still have some limitations, such as high reaction temperature, long reaction time. Therefore, the development of efficient methods for the synthesis of allyl-substituted quinolines/ isoquinolines is highly desired.

Previously, we reported the synthesis of substituted quinolines via electrophilic cyclization of 1-azido-2-(2-propynyl) benzenes in the presence of electrophilic reagents or electrophilic catalysts (Eq. 4) [10]. Also we reported metal-catalyzed or nonmetal-catalyzed synthesis of substituted dihydroisoquinolines, and iodine-mediated or gold-catalyzed synthesis of substituted isoquinolines (Eq. 5) [11]. Encouraged by the findings above, we have developed an effective strategy for the regioselective one-step synthesis of allylated quinolines via the palladium-catalyzed cyclization-allylation reaction of 1-azido-2-(2-propynyl) benzene **1** and allyl methyl carbonate **2a** [12]. The corresponding 3, 4-diallylquinoline **3a** in 69% yield in the case of R^4 = H and 3-allylquinoline **4** in 67% yield in the case of $R^4 \neq H$ were obtained in the presence of $Pd(PPh_3)_4$ and K_3PO_4 or NaOAc in DMF at 100 °C. In addition, we newly found that 1,4-diallylisoquinolines **6** and 4-allylisoquinolines **7** could also be synthesized from 2-alkynyl benzyl azides **5** and allyl methyl carbonate **2a** under mild reaction conditions. To the best of our knowledge, it is the first time for the one-step synthesis of 1,4-diallylisoquinolines **6** and 4-allylisoquinolines **7** via palladium-catalyzed cyclization-allylation of azides and allyl methyl carbonate to date. Furthermore, this palladium-catalyzed reaction is mechanistically interesting, compared to the Au^+-catalyzed and I^+-mediated reactions, as mentioned later. Herein, we report a detailed investigation of these synthetic methods for the allyl- and diallyl-substituted quinolines and isoquinolines.

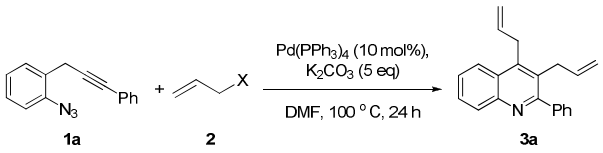
Results and Discussion

Synthesis of 3-allylquinolines and 3,4-diallylquinolines from azides and allyl methyl carbonate

Initially, we selected 1-azido-2-(3-phenylprop-2-ynyl) benzene **1a** as a model substrate to screen allyl sources. The results are summarized in Table 1. When allyl methyl carbonate **2a** was used, the reaction proceeded smoothly and gave the desired 3, 4-diallylquinoline **3a** in 47% isolated yield (entry 1). Allyl chloride **2b** produced the desired product **3a** in low yield (entry 2). No desired product was obtained with allyl tributyltin **2c** (entry 3). Allyl acetate **2d**, giving the product **3a** in 39% isolated yield together with unidentified products (entry 4). Also, the use of **2a** together with **2d** produced **3a** in lower yield (entry 5). Thus, allyl methyl carbonate was utilized as an allyl source for further optimization of reaction conditions.

Our research focused on the optimization of palladium catalysts, solvents, bases and temperatures, and the results are summarized in Table 2. No desired product **3a** was obtained in the absence of palladium catalyst (entry 1). A yield of 26% was obtained when the reaction was carried out in the presence of $Pd(PPh_3)_4$ but in the absence of base (entry 5). This result indicated the importance of the combined use of both palladium catalyst and base. Next we tested two palladium catalysts, $Pd_2(dba)_3{\cdot}CHCl_3$ and $Pd(PPh_3)_4$, respectively (entries 2-4 and 6), the latter gave a much better result. The use of ligands, XantPhos and S-Phos, gave 8% and 35% yields in the presence of

Table1 Screening of the Allyl Sources.

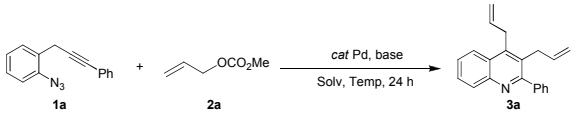


1a 2 3a

Entry	Allyl sources		3a, Yield (%) [a]
1	OCO_2Me	**2a**	52 (47) [b]
2	Cl	**2b**	23
3	$SnBu_3$	**2c**	0
4	OAc	**2d**	44 (39) [b]
5		**2a + 2d**	21 [c]

[a] ^{1}H NMR yield was determined by using *p*-xylene as an internal standard. [b] Isolated yield is shown in parentheses. [c] 2.5 eq 2a and 2.5 eq 2d were used respectively.

Table 2 Optimization of the Reaction Conditions [a]



1a 2a 3a

Entry	*cat* Pd	Bases	Solvent	Yield (%) [b]	SM recov. (%) [b]
1	-	K_3CO_3	DMF	0	0
2	$Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%)	K_3CO_3	DMF	4	0
3	$Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) [c]	K_3CO_3	DMF	8	0
4	$Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) [d]	K_3CO_3	DMF	35	0
5	$Pd(PPh_3)_4$	-	DMF	26	0
6	$Pd(PPh_3)_4$	K_2CO_3	DMF	(47) [e]	0
7	$Pd(PPh_3)_4$	Na_2CO_3	DMF	42	0
8	$Pd(PPh_3)_4$	$NaHCO_3$	DMF	46	0
9	$Pd(PPh_3)_4$	NaOH	DMF	56	0
10	$Pd(PPh_3)_4$	NaOAc	DMF	66	0
11	$Pd(PPh_3)_4$	K_3PO_4	DMF	75 (69) [e]	0
12	$Pd(PPh_3)_4$	KH_2PO_4	DMF	37	0
13	$Pd(PPh_3)_4$	Et_3N	DMF	48	0
14	$Pd(PPh_3)_4$	K_3PO_4	1,4-dioxane	27	5
15	$Pd(PPh_3)_4$	K_3PO_4	AcOEt	29	8
16	$Pd(PPh_3)_4$	K_3PO_4	Benzene	26	11
17	$Pd(PPh_3)_4$	K_3PO_4	CH_3CN	66	0
18	$Pd(PPh_3)_4$	K_3PO_4	CH_3CN+H_2O	15	0
19	$Pd(PPh_3)_4$	K_3PO_4	THF	30	8
20	$Pd(PPh_3)_4$ [f]	K_3PO_4	DMF	69 (60) [e]	0
21	$Pd(PPh_3)_4$ (5 mol%)	K_3PO_4	DMF	63	0
22	$Pd(PPh_3)_4$	K_3PO_4 (3 eq)	DMF	65 (59) [e]	0

[a] The reactions were performed with **1a** (0.05 mmol) and **2a** (5 eq) in the presence of Pd catalyst (10 mol%) and base (5 eq) in 1mL DMF at 100 °C for 24 h under a argon atmosphere. [b] ^{1}H NMR yield was determined by using *p*-xylene as an internal standard. [c] 5 mol% XantPhos was used. [d] 10 mol% S-Phos was used. [e] Isolated yield is shown in parentheses. [f] The reaction temperature was 80 °C .

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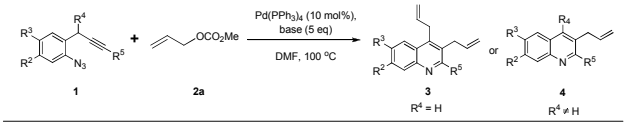
$Pd_2(dba)_3{\cdot}CHCl_3$, respectively (entries 3 and 4). Among the various bases we investigated (entries 6-13), the use of K_3PO_4 and NaOAc afforded **3a** in high yields (entries 10 and 11). The screening of various solvents, such as 1, 4-dioxane, AcOEt, benzene, CH_3CN, CH_3CN+H_2O, THF and DMF, revealed that solvents played an important role in the formation of **3a** (entries 11, 14-19). DMF was found to be the most suitable solvent, and the product **3a** was obtained in 69% isolated yield (entry 11). The decrease in reaction temperature to 80 °C gave the product **3a** in 60% isolated yield (entry 20). Decreasing the amounts of base and catalyst resulted in lower yields (entries 21 and 22).

Table 3 Synthesis of 3,4-diallylquinolines with various substrates [a]

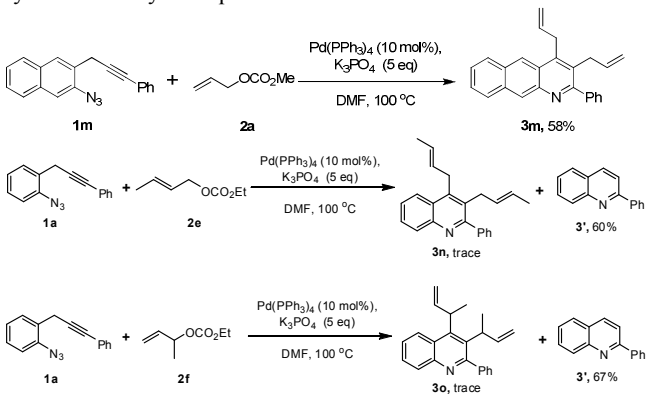


1 2a 3 (R^4 = H) 4 ($R^4 \neq$ H)

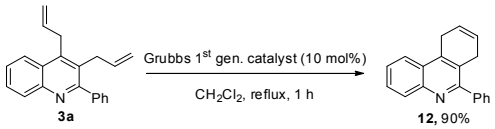
Entry	Substrate **1**	R^2	R^3	R^4	R^5	Methods	**3** or **4**	Time (h)	Yield (%) [b]
1	**1a**	H	H	H	Ph	A	**3a**	5	69
2	**1b**	H	H	H	*p*-Me-Ph	A	**3b**	4	66
3	**1c**	H	H	H	3,5-F_2-Ph	A	**3c**	3	55
4	**1d**	H	H	H	cyclohexyl	B	**3d**	24	38
5	**1e**	H	H	H	3-Me-Ph	A	**3e**	5	60
6	**1f**	H	H	H	*p*-Cl-Ph	A	**3f**	5	64
7	**1g**	H	Br	H	*p*-Me-Ph	A	**3g**	5	42
8	**1h**	H	Br	H	Ph	B	**3h**	2	45
9	**1i**	H	Cl	H	Ph	A	**3i**	5	33
10	**1j**	H	H	H	H	A	-	5	n.d [c]
11	**1k**	H	H	OAc	Ph	B	**4**	5	67

[a] All the reactions were carried out using 0.05 mmol of **1** and 5 eq of **2** in the presenc of $Pd(PPh_3)_4$ (10 mol%) under argon atomosphere in 1mL DMF at 100 °C; method A, DMF (1 mL), K_3PO_4 (5 eq); method B, NaOAc (5 eq). [b] Isolated yield. [c] Not determined.

With the optimized conditions in hand, we carried out the reactions between various 1-azido-2-(2-propynyl) benzenes **1** and allyl methyl carbonate **2a**, and the results are summarized in Table 3. The substrate **1b**, having a methyl at the *para*-position of the aromatic ring, afforded the corresponding cyclized product **3b** in 66% isolate yield through method A (entry 2). The substrate **1c**, bearing fluorine atoms at 3,5-positions on the aromatic ring, afforded the desired product **3c** in 55% yield (entry 3). Furthermore, the substrates **1d**, having a cyclohexyl group at the alkyne terminus, gave the expected products **3d** in moderate yields with method B (entries 4); Here, a mixture of unidentified by-products were formed, but they were easily separated from the desired quinoline by column chromatography. It is noteworthy that the method B gave a little higher yield than the method A, although it took a longer reaction time. The substrates **1e** and **1f**, having a methyl at the *meta*-position and a chloro group at *para*-position of the aromatic ring, afforded products **3e** and **3f** in 60% and 64% isolate yield through method A (entries 5 and 6). The substrates **1g, 1h** and **1i**, in which the aromatic ring was substituted with bromo and chloro groups, afforded the corresponding products **3g**, **3h** and **3i** in moderate yields, respectively (entries 7-9). The reaction led to a mixture and no products **3** and/or **4** were observed when substrate **1j** (R^5 = H) reacted with **2a** (entry 10). It is noteworthy that the reaction of **1k**, having OAc group at R^4 (at the benzylic position), proceeded smoothly and gave the 3-allylquinoline **4** in 67% isolated yield (entry 11). The substrate **1m** afforded the desired product **3m** in 58% yield with method B. On the basis of the results above, it clearly indicated that R^4 group plays a key role in the selective synthesis of allylated quinolines.



Other substituted allyl carbonates such as crotyl ethyl carbonate **2e** and ethyl 2-methylallyl carbonate **2f,** instead of allyl methyl carbonate **2a,** were also investigated and gave only trace amounts of the products **3n** and **3o**. 2-phenylquinoline **3'** as main product [10] was formed. Next, we investigated the feasibility of the ring closing metathesis reaction [13] of **3a**. The reaction of **3a** was carried out in CH_2Cl_2 at reflux for 1 h in the presence of 10 mol% Grubbs' first generation catalyst and obtained the desired cyclization product **12** in 90% yield.



A proposed mechanism for the formation of 3,4-diallylquinoline **3a** via palladium-catalyzed cyclization-allylation reaction of 1-azido-2-(2-propynyl) benzene **1a** and allyl methyl carbonate **2a** is illustrated in Scheme 2. Initially, Pd(0) reacts with allyl methyl carbonate **2a** to form the π-allyl palladium species **8** [14, 15] with concomitant evolution of CO_2. Deprotonation of propargylic proton of **1a** takes place with methoxide formed. Then nucleophilic attack of propargylic anion to allylpalladium cation to result in propargylic allylation **9** and regeneration of Pd(0). Next, oxidative addition of allyl methyl carbonate **2a** occurs again to form **8**, the intermediate **9** reacts with **8** again to generate intermediate **10** and subsequent nucleophilic attack of a nitrogen atom to the electron-deficient alkyne forms an intermediate **11**. Finally, elimination of N_2 and H^+, together with elimination of Pd (0), produces 3,4-diallylquinoline **3a**. It is noteworthy that, for the azide-alkyne cyclization, Pd (II) acts similarly as I^+ reagent, Bronsted acid and Au catalyst. Perhaps, the most important point of the present Pd methodology, compared to the previous Au^+ and I^+ methods,[13] is that the Pd-catalyzed azide-alkyne cyclization is able to incorporate another organic ligand of Pd (see **9**), which is allyl in present, into quinoline framework.

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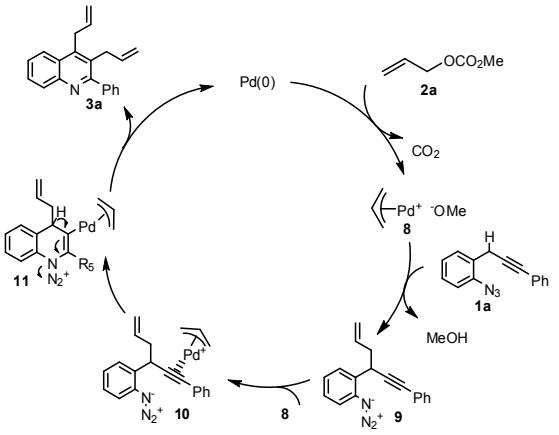
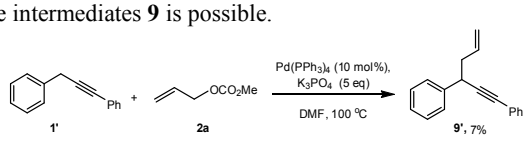


Scheme 2 A Proposed Mechanism for the Formation of **3a**.

On the basis of the proposed mechanism in Scheme 2, we conducted some the experiments under the optimized reaction conditions to investigate the formation of the intermediates in this process. Firstly, allylated alkyne **9** as starting material was prepared in order to investigate the feasibility for the synthesis of 3,4-diallylquinoline **3a**. However, we did not get compound **9** at all. Next, the substrate **1'** without azide was used to test if the similar allylation product **9'** would be formed. As a result, compound **9'** was observed in mixture and gave 7% NMR yield by ^{1}H NMR and GC-MS. The result suggests that the formation of the intermediates **9** is possible.

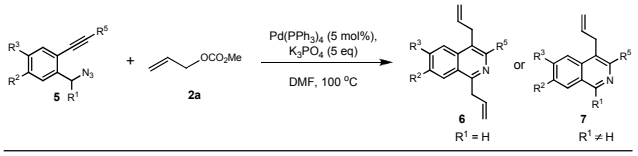


Synthesis of 4-allylisoquinolines and 1,4-diallylisoquinolines from azides and allyl methyl carbonate

Encouraged by the successful synthesis of 3-allylquinoline **4** and 3,4-diallylquinolines **3a**, we used 2-alkynyl benzyl azides **5** as starting materials, instead of 1-azido-2-(2-propynyl) benzene **1a**, to synthesize 4-allylisoquinolines **7** and 1,4-diallylisoquinolines **6**. The similar reaction conditions in the synthesis of allylated quinoline are also effective for isoquinoline synthesis (see Table S1 in supporting information).

The scopes of the cyclization-allylation reactions of 2-alkynyl benzyl azides **5** and allyl methyl carbonate **2a** are examined, and the results are summarized in Table 4. Firstly, the reactions for the synthesis of 1,4-diallylisoquinolines are carried out when R^1 = H (entries 1-5). An arylacetylene bearing a methoxy group **5b** on the aromatic ring afforded the corresponding product **6b** in 51% yield (entry 2). The substrates **5c**, in which the aromatic ring was substituted with chloro group, gave the product **6c** in 55% yield (entry 3). The reaction of **5d**, having 1-cyclohexenyl substituent at R^5 gave the corresponding product **6d** in 41% yield (entry 4). The substrates **5e,** having a 3,4-di-RO substituent on the aromatic ring gave the product **6e** in 52% yield (entry 5). Next, synthesis

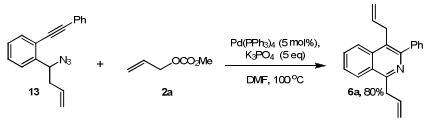
Table 4 Synthesis of Allylisoquinolines with Various Substrates [a]



Entry	Substrate **5**	R^1	R^2	R^3	R^5	**6** or **7**	Time (h)	Yield (%) [b]
1	**5a**	H	H	H	Ph	**6a**	5	86
2	**5b**	H	H	H	*p*-OMe-Ph	**6b**	14	51
3	**5c**	H	Cl	H	Ph	**6c**	4	55
4	**5d**	H	H	H	1-cyclohexenyl	**6d**	5	41
5	**5e**	H	—O—CH_2—O—		Ph	**6e**	5	52
6	**5f**	Me	H	H	Ph	**7a**	2	85
7	**5g**	Ph	H	H	Ph	**7b**	5	93
8	**5h**	Ph	Cl	H	Ph	**7c**	5	87
9	**5i**	Ph	H	H	cyclohexyl	**7d**	5	79
10	**5j**	Me	—O—CH_2—O—		Ph	**7e**	12	81
11	**5k**	Me	—O—CH_2—O—		*p*-tolyl	**7f**	5	90
12	**5m**	Ph	—O—CH_2—O—		*p*-Cl-Ph	**7g**	10	60
13	**5n**	Me	H	H	*p*-F-Ph	**7h**	3	93
14	**5o**	Ph	H	H	3-Me-Ph	**7i**	3	89

[a] All the reactions were carried out using **5** (0.05 mmol) and **2a** (5 eq) in the presenc of $Pd(PPh_3)_4$ (5 mol%) under argon atomosphere in 1mL DMF at 100 °C; . [b] Isolated yield.

of 4-allylisoquinolines **7** are investigated using more highly substituted substrates when $R^1 \neq$ H (entries 6-14). The **5f** and **5g** substituted with methyl and phenyl groups at R^1 position proceeded without problems and gave products **7a** and **7b** in 85% and 93% yields, respectively (entries 6 and 7). The substrate **5h** gave the product **7c** in 87% yield (entry 8). The reaction of **5i**, having cyclohexyl group at R^5 gave the corresponding product **7d** in 79% yield (entry 9). The substrates **5j**, **5k** and **5m** having 3,4-di-RO substituents on the aromatic ring gave the products **7e, 7f** and **7g** in 81%, 90% and 60% yields, respectively (entries 10, 11 and 12). The reactions of **5n** and **5o**, having methyl and phenyl groups at R^1 position gave the corresponding product **7h** and **7i** in 93% and 89% yields, respectively (entry 13 and 14). A substrate **13**, having allyl group at R^1 proceeded smoothly and gave products **6a** in 80% yield. From the results above, we found that the substrates (R^1 = H) gave less yields than the more highly substituted substrates ($R^2 \neq$ H). The observations might indicate that the palladium-catalyzed cyclization-allylation reaction is able to incorporate another organic ligand of Pd (see **13** in Scheme 3), which is allyl in present, into isoquinoline framework.



Two substituted allyl carbonates such as crotyl ethyl carbonate **2e** and ethyl 2-methylallyl carbonate **2f,** instead of allyl methyl carbonate **2a,** were also investigated. Unfortunately, the allyl sources **2e** and **2f** are ineffective for the substrates **5a** and **5k**, and only trace amounts of the diallyl-substituted isoquinolines and allyl-substituted isoquinolines were detected in the mixture by ^{1}H NMR and GC-MS analysis.

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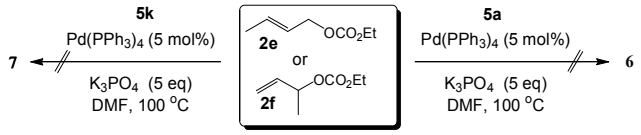
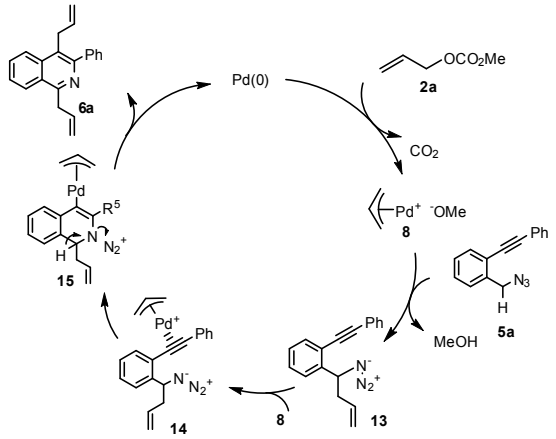
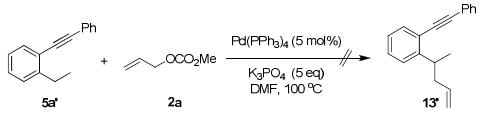


A plausible reaction pathway for the synthesis of 1,4-diallylisoquinoline **6a** via Pd-catalyzed cyclization-allylation reaction of 2-alkynyl benzyl azide **5a** and allyl methyl carbonate **2a** is shown in Scheme 3. Similar to the previous observation in the synthesis of compounds **3a** (see Scheme 2), initially, Pd(0) reacts with allyl methyl carbonate **2a** to form the π-allyl palladium species **8** [14, 15] with concomitant evolution of CO_2. Deprotonation of benzylic proton of **5a** takes place with methoxide formed. Then nucleophilic attack of benzylic anion to allylpalladium cation to result in benzylic allylation **13** and regeneration of Pd(0) [16]. Next, oxidative addition of allyl carbonate **2a** occurs again to form **8**, the intermediate **13** reacts with **8** again to generate intermediate **14** and subsequent nucleophilic attack of a nitrogen atom to the electron-deficient alkyne forms an intermediate **15**. Finally, elimination of N_2 and H^+, together with elimination of Pd (0), produces 1,4-diallylisoquinoline **6a**.



Scheme 3 A Plausible Reaction Pathway for the Formation of **6a**.

As mentioned above, the reaction of the compound **13** proceeded smoothly and gave **6a** in 80% yield under the optimized conditons. It showed that the formation of the intermediate **13** in this process is possible. Next, the reaction of **5a'** was carried out in order to investigate the role of the azide group in this process, no expected compound 13' was observed in the absence of azide group. It indicated that the electron-withdrawing effect of azide moiety is necessary for the allylation process.



Conclusion

We have first developed an effective strategy for the regioselective one-step synthesis of allylated quinolines/isoquinolines via the palladium-catalyzed cyclization-allylation reaction of azides and allyl methyl carbonate. As a result, allylated quinolines/isoquinolines were obtained in good to high yields. R^1 and R^4 groups play a key role for the transformation. Diallyl-substituted quinolines/ isoquinolines are achieved when $R^1 = R^4 = H$, while allyl-substituted quinolines/ isoquinolines are achieved when $R^1 \neq H$ and $R^4 \neq H$. The present studies provide useful methods for the synthesis of allylated quinolines/isoquinolines with a wide variety of substrates. Further works to expand the scope and synthetic utility of this methodology to the synthesis of biologically important natural and unnatural compounds are in progress.

Experimental Section

General Information

^1H and ^{13}C NMR spectra were operated at 400 MHz and 100 MHz, respectively. The reactions were monitored by thin-layer chromatography (TLC). Column chromatography was performed on neutral silica gel (60N, 45-75 μm) and hexane/AcOEt (5:1) was used as an eluent. The $Pd(PPh_3)_4$ was prepared according to the literature procedure. [17] All starting materials used in our study were prepared in the laboratory. Substrates **5a-5o** were prepared according to the reported literatures. [11b, 11d] The procedures and analytical data of **5a**, **5b**, **5d**, **5f**, **5g** and **5j-5k** should be seen in our prevous literatures. [11b, 11d] Substrate **5a'** was prepared according to the reported literatures. [18] TLC was performed on aluminum-precoated plates of silica gel 60 with an HSGF254 indicator and visualized under UV light or developed by immersion in the solution of 0.6% $KMnO_4$ and 6% K_2CO_3 in water.

2-(azidomethyl)-4-chloro-1-(phenylethynyl)benzene (5c). Yellow oil (883.4 mg, 33%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.61 (s, 2H), 7.33-7.29 (t, *J* = 8.2 Hz, 1H), 7.40-7.34 (m, 3H), 7.41 (s, 1H), 7.50-7.46 (d, *J* = 7.2 Hz, 1H), 7.58-7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8, 85.5, 95.5, 121.1, 122.5, 128.4, 128.5, 128.5, 128.9, 131.6, 133.5, 134.6, 139.0. IR (KBr) 3058, 2923, 2098, 1496, 1259, 1103, 825, 750, 686 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{15}H_{11}N_3Cl$ $[M + H]^+$ 268.0642; Found 268.0639.

5-(azidomethyl)-6-(phenylethynyl)benzo[d][1,3]dioxole (5e). Yellow oil (804.1 mg, 29%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 2H), 6.02 (s, 2H), 6.87 (s, 1H), 7.01 (s, 1H), 7.38-7.33 (m, 3H), 7.57-7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 86.7, 93.1, 101.7, 109.1, 111.8, 116.2, 122.9, 128.4, 128.4, 131.5, 132.1, 147.4, 148.3. IR (KBr) 3046, 2902, 2098, 1479, 1375, 1218, 1039, 929, 750 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{16}H_{12}N_3O_2$ $[M + H]^+$ 278.0930; Found 278.0931.

2-(azido(phenyl)methyl)-4-chloro-1-(phenylethynyl)benzene (5h). Yellow oil (859.5 mg, 25%); ^1H NMR (400 MHz, $CDCl_3$), δ 6.29 (s, 1H), 7.30-7.27 (d, *J* = 8.2 Hz, 1H), 7.40-7.35 (t, *J* = 4.2, Hz, 8H), 7.50-7.45 (t, *J* = 8.0 Hz, 3H), 7.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.9, 85.0, 95.9, 120.6, 122.5, 127.3, 127.5, 128.2, 128.3, 128.5, 128.8, 128.8, 131.5, 133.6, 134.9, 138.3, 143.1. IR (KBr) 3064, 2931, 2098, 1491, 1265, 1103, 814, 756, 692 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{21}H_{15}N_3Cl$ $[M + H]^+$ 344.0955; Found 344.0947.

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1-(azido(phenyl)methyl)-2-(cyclohexylethynyl)benzene (5i). colourless oil (504.7 mg, 16%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41-1.28 (m, 3H), 1.63-1.42 (m, 3H), 1.81-1.66 (m, 2H), 1.88 (d, *J* = 12.2, 2H), 2.63 (dd, *J* = 9.0, 3.5 Hz, 1H), 6.30 (s, 1H), 7.23-7.18 (m, 1H), 7.29-7.25 (m, 2H), 7.36-7.32 (m, 5H), 7.42 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 25.8, 29.8, 32.5, 65.9, 78.2, 100.3, 123.2, 126.9, 127.3, 127.7, 127.8, 128.0, 128.5, 132.4, 139.3, 141.0. IR (KBr) 3029, 2925, 2850, 2098, 1485, 1450, 1247, 750, 692 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1814; Found 316.1808.

5-(azido(phenyl)methyl)-6-((4-chlorophenyl)ethynyl)benzo[d][1,3]dioxole (5m). Yellow oil (1085.9 mg, 28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05-5.90 (m, 2H), 6.31 (s, 1H), 6.87 (s, 1H), 6.97 (s, 1H), 7.34-7.30 (m, 3H), 7.37-7.34 (m, 4H), 7.42-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.8, 88.0, 92.3, 101.8, 107.7, 111.5, 115.2, 126.4, 127.1, 127.4, 128.0, 128.8, 132.6, 133.7, 134.5, 139.2, 147.1, 148.7. IR (KBr) 2917, 2845, 2095, 1464, 1238, 1029, 869 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{22}H_{15}N_3O_2Cl$ $[M + H]^+$ 388.0853; Found 388.0864.

1-(1-azidoethyl)-2-((4-fluorophenyl)ethynyl)benzene (5n). colourless oil (955.0 mg, 36%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (d, *J* = 6.8, 3H), 5.26 (q, *J* = 6.8 Hz, 1H), 7.12-7.03 (m, 2H), 7.34-7.28 (m, 1H), 7.42-7.35 (m, 1H), 7.50-7.44 (m, 1H), 7.58-7.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 58.9, 86.3, 93.4, 119.0, 119.0, 121.5, 125.5, 127.7, 129.0, 132.5, 133.4, 133.5, 142.7. IR (KBr) 3066, 2982, 2089, 1506, 1232, 827, 756 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{16}H_{13}N_3F$ $[M + H]^+$ 266.1094; Found 266.1083.

1-(azido(phenyl)methyl)-2-(m-tolylethynyl)benzene (5o). Yellow oil (1811.0 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.37 (s, 1H), 7.19-7.16 (m, 1H), 7.31-7.27 (m, 5H), 7.41-7.33 (m, 5H), 7.49-7.45 (m, 1H), 7.57-7.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 66.1, 86.6, 95.1, 122.3, 122.6, 126.7, 127.0, 127.5, 127.8, 128.0, 128.3, 128.6, 128.8, 129.5, 132.1, 132.5, 138.1, 139.1, 141.3. IR (KBr) 2917, 2851, 2095, 1470, 869, 750, 691 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{22}H_{18}N_3$ $[M + H]^+$ 324.1501; Found 324.1517.

1-(1-azidobut-3-enyl)-2-(phenylethynyl)benzene (13). Yellow oil (519.3 mg, 19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72-2.55 (m, 2H), 5.21-5.15 (m, 2H), 5.29-5.24 (m, 1H), 5.96-5.80 (m, 1H), 7.35-7.29 (m, 1H), 7.43-7.36 (m, 4H), 7.51-7.45 (m, 1H), 7.62-7.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 63.4, 86.6, 94.7, 118.3, 121.8, 122.8, 126.0, 127.7, 128.4, 128.6, 128.8, 131.5, 132.4, 133.8, 141.2. IR (KBr) 2917, 2839, 2095, 1458, 910, 744, 685 cm^{-1}. HRMS-ESI (m/z) $[M]^+$ Calcd for $C_{18}H_{16}N_3$ $[M + H]^+$ 274.1344; Found 274.1336.

General Procedure for the Synthesis of 1,4-diallylquinoline (6)

To a 5-mL screw-capped vial equipped with a magnetic stirring bar were added 1-(azidomethyl)-2-(phenylethynyl)benzene **5a-5e** (0.05 mmol), $Pd(PPh_3)_4$ (2.9 mg, 0.0025 mmol), K_3PO_4 (53.1 mg, 0.25 mmol), allyl methyl carbonate **2a** (28.4 μL, 0.25 mmol), and DMF (1 mL). The mixture was stirred at 100 °C. The reaction progress was monitored by TLC (hexane/ethyl acetate, 5/1). After consumption of the staring material, the reaction mixture was cooled to room temperature and filtered through a short column with the use of ethyl acetate as eluent. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 30/1~5/1) to provide the product **6a-6e**.

1,4-diallyl-3-phenylisoquinoline (6a). Yellow oil (12.3 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (dd, *J* = 14.1, 6.6 Hz, 2H), 3.12 (dd, *J* = 14.1, 7.8 Hz, 2H), 5.10-4.78 (m, 4H), 5.37-5.22 (m, 2H), 7.49-7.36 (m, 4H), 7.53 (t, J = 7.7 Hz, 2H), 7.93-7.85 (m, 1H), 8.02-7.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.0, 71.2, 120.4, 121.2, 123.1, 127.0, 127.7, 127.7, 128.1, 128.3, 128.29, 128.7, 128.9, 128.9, 130.1, 131.5, 137.2, 139.3, 148.1. IR (KBr) 3075, 2919, 2850, 1641, 1450, 1352, 982, 923, 756, 698 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{21}H_{18}N$ $[M - H]^+$ 284.1439; Found 284.1436.

1,4-diallyl-3-(4-methoxyphenyl)isoquinoline (6b). Yellow oil (8.0 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (dd, *J* = 14.1, 6.6 Hz, 2H), 3.10 (dd, *J* = 14.2, 7.8 Hz, 2H), 3.88 (s, 3H), 5.03-4.82 (m, 4H), 5.44-5.21 (m, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 7.50-7.37 (m, 3H), 7.95-7.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.1, 55.4, 71.1, 114.3, 120.3, 121.0, 123.1, 124.1, 128.0, 128.0, 128.1, 128.3, 128.4, 128.7, 128.7, 130.2, 139.2, 139.2, 148.0, 159.6. IR (KBr) 3071, 2914, 2848, 1727, 1612, 1503, 1357, 1248, 1030, 915, 828, 769 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{22}H_{20}NO$ $[M - H]^+$ 314.1545; Found 314.1544.

1,4-diallyl-7-chloro-3-phenylisoquinoline (6c). Yellow oil (8.8 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (dd, *J* = 14.1, 6.6 Hz, 2H), 3.12 (dd, *J* = 14.2, 7.8 Hz, 2H), 5.08-4.87 (m, 4H), 5.37-5.24 (m, 2H), 7.46-7.37 (m, 3H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.79 (t, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.9, 71.2, 120.9, 122.1, 123.6, 126.4, 127.0, 128.3, 128.5, 129.0, 129.0, 129.1, 129.6, 129.7, 131.2, 134.3, 136.3, 139.4, 149.9. IR (KBr) 3081, 2907, 2844, 1641, 1444, 1346, 982, 774, 692 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{21}H_{17}NCl$ $[M - H]^+$ 318.1050; Found 318.1047.

1,4-diallyl-3-cyclohexenylisoquinoline (6d). Yellow oil (5.9 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78-1.70 (m, 2H), 1.88-1.79 (m, 2H), 2.35-2.27 (m, 2H), 2.72-2.63 (m, 2H), 2.89 (dd, *J* = 14.0, 6.8 Hz, 2H), 3.05 (dd, *J* = 14.1, 7.8 Hz, 2H), 5.08-4.82 (m, 4H), 5.31-5.20 (m, 2H), 6.55-6.43 (m, 1H), 7.45-7.35 (m, 3H), 7.78-7.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.6, 25.6, 27.2, 29.7, 43.1, 70.7, 120.2, 121.5, 122.9, 126.8, 127.8, 128.2, 128.5, 128.6, 129.2, 130.2, 136.2, 139.6, 141.4, 147.9. IR (KBr) 3075, 2925, 2856, 1727, 1641, 1450, 993, 923, 762 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{21}H_{22}N$ $[M - H]^+$ 288.1752; Found 288.1755.

5,8-diallyl-7-phenyl-[1,3]dioxolo[4,5-g]isoquinoline (6e). Yellow oil (8.6 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (dd, *J* = 14.1, 6.6 Hz, 2H), 3.07 (dd, *J* = 14.1, 7.7 Hz, 2H), 5.08-4.87 (m, 4H), 5.37-5.26 (m, 2H), 6.08 (s, 2H), 6.88 (s, 1H), 7.30 (s, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.1, 70.9, 102.0, 102.2, 104.2, 120.4, 121.3, 126.9, 127.9, 128.9, 128.9, 130.1, 130.1, 131.6, 131.6, 137.1, 138.1, 142.3, 148.1, 148.2. IR (KBr) 3081, 2913, 1641, 1467, 1352, 1271, 1039, 918, 779, 692 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{22}H_{18}NO_2$ $[M - H]^+$ 328.1338; Found 328.1333.

General Procedure for the Synthesis of 4-allyl-1-methyl-3-phenylisoquinoline (7)

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To a 5-mL screw-capped vial equipped with a magnetic stirring bar were added 1-(azidomethyl)-2-(phenylethynyl)benzene **5f-5k** (0.05 mmol), $Pd(PPh_3)_4$ (2.9 mg, 0.0025 mmol), K_3PO_4 (53.1 mg, 0.25 mmol), allyl methyl carbonate **2a** (28.4 μL, 0.25 mmol), and DMF (1 mL). The mixture was stirred at 100 °C. The reaction progress was monitored by TLC (hexane/ethyl acetate, 5/1). After consumption of the staring material **5f-5k**, the reaction mixture was cooled to room temperature and filtered through a short column with the use of ethyl acetate as eluent. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 30/1~5/1) to provide the product **7a-7f.**

4-allyl-1-methyl-3-phenylisoquinoline (7a). Yellow oil (11.0 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.92 (dd, J = 14.1, 6.6 Hz, 1H), 3.05 (dd, J = 14.1, 7.9 Hz, 1H), 5.03-4.87 (m, 2H), 5.39-5.28 (m, 1H), 7.49-7.36 (m, 4H), 7.53 (t, J = 7.7 Hz, 2H), 7.88 (t, J = 7.3 Hz, 1H), 7.97 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 44.4, 120.3, 121.2, 122.7, 126.9, 127.1, 128.1, 128.4, 128.7, 128.9, 128.9, 130.4, 131.5, 136.4, 139.5, 150.2. IR (KBr) 3070, 2982, 2925, 1641, 1444, 1352, 988, 918, 762, 692 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{19}H_{16}N$ $[M - H]^+$ 258.1283; Found 258.1279.

4-allyl-1,3-diphenylisoquinoline (7b). Yellow oil (14.9 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (dd, J = 14.0, 6.4 Hz, 1H), 3.59 (dd, J = 14.0, 7.7 Hz, 1H), 5.02-4.82 (m, 2H), 5.23-5.12 (m, 1H), 7.49-7.30 (m, 9H), 7.54 (t, J = 7.5 Hz, 2H), 7.93 (d, J = 7.5 Hz, 1H), 8.01 (d, J = 7.7 Hz 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.2, 120.7, 121.3, 124.2, 126.0, 127.1, 128.2, 128.5, 128.5, 128.8, 128.8, 128.9, 129.0, 130.0, 131.4, 137.4, 139.1, 139.5, 139.5, 149.4. IR (KBr) 3058, 2912, 1646, 1491, 1444, 1352, 982, 756, 698 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{24}H_{18}N$ $[M - H]^+$ 320.1439; Found 320.1441.

4-allyl-7-chloro-1,3-diphenylisoquinoline (7c). Yellow oil (15.5 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (dd, J = 14.1, 6.4 Hz, 1H), 3.58 (dd, J = 14.1, 7.7 Hz, 1H), 5.06-4.84 (m, 2H), 5.23-5.13 (m, 1H), 7.47-7.30 (m, 8H), 7.58-7.50 (m, 2H), 7.84 (d, J = 8.2 Hz, 1H), 7.96 (t, J = 7.8 Hz 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.0, 121.2, 122.2, 124.6, 125.6, 125.9, 125.9, 127.0, 128.4, 128.8, 128.8, 129.0, 129.1, 129.5, 131.1, 134.6, 136.6, 138.5, 139.6, 151.2. IR (KBr) 3064, 2919, 1635, 1496, 1450, 1352, 982, 768, 698 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{24}H_{17}NCl$ $[M - H]^+$ 354.1050; Found 354.1053.

4-allyl-3-cyclohexyl-1-phenylisoquinoline (7d). Yellow oil (12.9 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54-1.30 (m, 3H), 1.84-1.69 (m, 3H), 1.91 (d, J = 12.9 Hz, 2H), 2.15-2.05 (m, 2H), 3.05 (t, J = 12.0 Hz, 1H), 3.36 (dd, J = 14.0, 6.3 Hz, 1H), 3.49 (dd, J = 14.0, 7.7 Hz, 1H), 4.97-4.76 (m, 2H), 5.18-5.06 (m, 1H), 7.36-7.28 (m, 6H), 7.46-7.38 (m, 2H), 7.67 (d, J = 7.6 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 26.5, 32.6, 36.3, 43.3, 120.4, 121.5, 124.1, 126.0, 127.5, 127.7, 128.3, 128.3, 128.6, 128.9, 130.1, 137.0, 139.4, 144.3, 148.9. IR (KBr) 3064, 2931, 2856, 1641, 1444, 1334, 988, 750, 692 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{24}H_{24}N$ $[M - H]^+$ 326.1909; Found 326.1911.

8-allyl-5-methyl-7-phenyl-[1,3]dioxolo[4,5-g]isoquinoline (7e). Yellow oil (12.3 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H), 2.85 (dd, J = 14.0, 6.6 Hz, 1H), 3.00 (dd, J = 14.0, 7.8 Hz, 1H), 5.06-4.87 (m, 2H), 5.43-5.28 (m, 1H), 6.07 (s, 2H), 6.88 (s, 1H), 7.31 (s, 1H), 7.38 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.89 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 44.4, 101.9, 102.2, 103.9, 120.3, 120.4, 126.9, 127.9, 128.9, 130.3, 130.4, 131.6, 136.4, 138.3, 144.5, 148.1, 148.3. IR (KBr) 3070, 2913, 2844, 1646, 1467, 1352, 1294, 1033, 698 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{20}H_{16}NO_2$ $[M - H]^+$ 302.1181; Found 302.1176.

8-allyl-5-methyl-7-p-tolyl-[1,3]dioxolo[4,5-g]isoquinoline (7f). Yellow oil (14.3 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H), 2.43 (s, 3H), 2.85 (dd, J = 14.0, 6.6 Hz, 1H), 2.99 (dd, J = 14.0, 7.8 Hz, 1H), 5.06-4.84 (m, 2H), 5.45-5.28 (m, 1H), 6.06 (s, 2H), 6.88 (s, 1H), 7.36-7.27 (m, 3H), 7.78 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 25.6, 44.4, 101.9, 102.1, 103.9, 120.2, 120.6, 126.8, 128.7, 129.6, 130.4, 130.4, 136.1, 137.8, 138.3, 144.4, 148.1, 148.1. IR (KBr) 3075, 2982, 2919, 1745, 1601, 1473, 1352, 1294, 1039, 923, 819, 692 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{21}H_{18}NO_2$ $[M - H]^+$ 316.1338; Found 316.1341.

8-allyl-7-(4-chlorophenyl)-5-phenyl-[1,3]dioxolo[4,5 g]isoquin -oline (7g). Yellow oil (12.0 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (dd, J = 14.1, 6.4 Hz, 1H), 3.55 (dd, J = 14.1, 7.6 Hz, 1H), 5.04-4.84 (m, 2H), 5.25-5.14 (m, 1H), 6.13-6.00 (m, 2H), 6.88 (s, 1H), 7.29-7.26 (m, 1H), 7.39-7.30 (m, 5H), 7.53-7.46 (m, 2H), 7.86 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.0, 102.0, 102.1, 105.3, 120.3, 120.9, 126.0, 128.2, 128.6, 129.0, 129.1, 129.2, 129.9, 130.0, 133.8, 137.1, 137.5, 139.0, 143.9, 148.3, 148.6. IR (KBr) 2905, 1470, 1345, 1029, 928, 827, 732 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{25}H_{17}NO_2Cl$ $[M - H]^+$ 398.0943; Found 398.0943.

4-allyl-3-(4-fluorophenyl)-1-methylisoquinoline (7h). Yellow oil (12.9 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.92 (dd, J = 14.1, 6.6 Hz, 1H), 3.04 (dd, J = 14.1, 7.9 Hz, 1H), 5.04-4.88 (m, 2H), 5.39-5.28 (m, 1H), 7.28-7.17 (m, 2H), 7.49-7.40 (m, 3H), 7.83 (t, J = 6.4 Hz, 1H), 7.97-7.89 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 44.3, 120.4, 121.0, 122.7, 122.8, 126.7, 127.7, 127.7, 128.5, 128.7, 128.8, 130.3, 130.3, 136.2, 138.6, 150.1. IR (KBr) 2911, 2845, 1506, 1220, 833, 756, 577 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{19}H_{15}NF$ $[M - H]^+$ 276.1189; Found 276.1190.

4-allyl-1-phenyl-3-m-tolylisoquinoline (7i). Yellow oil (14.9 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.37 (dd, J = 14.0, 6.2 Hz, 1H), 3.52 (dd, J = 14.0, 7.7 Hz, 1H), 4.98-4.74 (m, 2H), 5.16-5.05 (m, 1H), 7.22-7.14 (m, 1H), 7.44-7.22 (m, 9H), 7.72 (d, J = 7.6 Hz, 1H), 7.80 (s, 1H), 7.86 (d, J = 5.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 43.1, 120.7, 121.3, 124.1, 124.2, 126.0, 127.1, 127.8, 127.9, 128.5, 128.8, 129.0, 130.0, 131.3, 137.4, 137.5, 138.6, 138.7, 139.2, 139.2, 139.6, 149.4. IR (KBr) 2911, 2851, 1589, 1446, 1220, 916, 658 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{25}H_{20}N$ $[M - H]^+$ 334.1596; Found 334.1592.

General Procedure for the ring closing reaction (12)

To a 5-mL screw-capped vial equipped with a magnetic stirring bar were added 3,4-diallylquinolines 3**a** (14.3 mg, 0.05 mmol), Grubbs I catalyst (4.1 mg, 0.005 mmol), and CH_2Cl_2 (1 mL). The mixture was stirred for 1 h at 40 °C. The reaction progress was monitored by TLC (hexane/ethyl acetate, 10/1). After consumption of the staring material **3a**, the reaction mixture was

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cooled to room temperature and filtered through a short column with the use of ethyl acetate as eluent. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 30/1~5/1) to provide the product **12** in 90% yield as a yellow oil (11.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95-2.83 (m, 2H), 3.38-3.25 (m, 2H), 6.17-6.02 (m, 2H), 7.39-7.29 (m, 2H), 7.53-7.40 (m, 4H), 7.90-7.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.8, 47.0, 112.2, 123.3, 126.2, 127.8, 128.0, 128.3, 128.8, 128.9, 129.9, 130.0, 130.7, 134.8, 140.0, 144.0, 148.3. IR (KBr) 3058, 2919, 2844, 1635, 1253, 1033, 796 cm^{-1}. HRMS-EI (m/z) $[M]^+$ Calcd for $C_{19}H_{14}N$ $[M-H]^+$ 256.1126; Found 256.1122.

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