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Iridium-Catalyzed Allylic Vinylation and Asymmetric Allylic Amination Reactions with *o*-Aminostyrenes

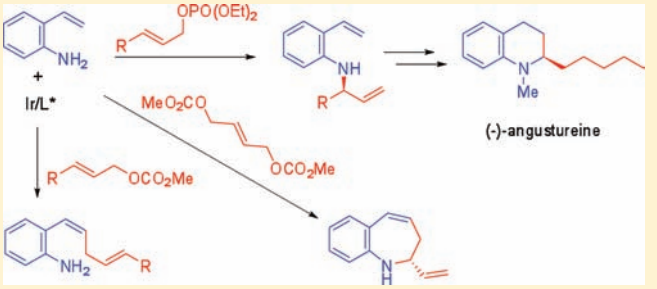
Ke-Yin Ye,[†] Hu He,[†] Wen-Bo Liu,[†] Li-Xin Dai,[†] Günter Helmchen,[‡] and Shu-Li You*[,†]

[†]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

[‡]Organisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Supporting Information

ABSTRACT: An Ir-catalyzed allylic vinylation reaction of allyl carbonates with *o*-aminostyrene derivatives has been realized, providing skipped (*Z*,*E*)-diene derivatives. With (*E*)-but-2-ene-1,4-diyl dimethyl dicarbonate as the substrate, an efficient enantioselective synthesis of 1-benzazepine derivatives via an Ir-catalyzed domino allylic vinylation/intramolecular allylic amination reaction has been developed. Mechanistic studies of the allylic vinylation reaction have been carried out, and the results suggest that the leaving group of the allylic precursor plays a key role in directing the reaction pathway. Screening of various allylic precursors showed that Ir-catalyzed reactions of allyl diethyl phosphates with *o*-aminostyrene derivatives proceed via an allylic amination pathway. A subsequent ring-closing metathesis (RCM) reaction of the amination products led to a series of enantiomerically enriched 1,2-dihydroquinoline derivatives. Their utility is indicated by an asymmetric total synthesis of (−)-angustureine.

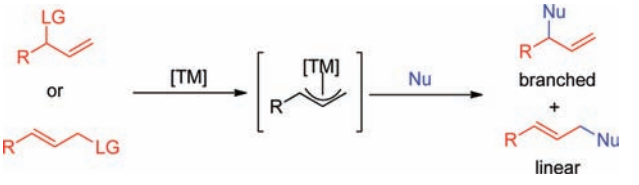


INTRODUCTION

Transition-metal-catalyzed allylic substitution reactions have been developed into powerful tools for constructing carbon−carbon and carbon−heteroatom bonds.[1] Palladium complexes have been the most-studied catalysts for asymmetric allylic substitution reactions. However, in the presence of a palladium catalyst, monosubstitued allyl derivatives yield π-allyl complexes that preferentially lead to achiral linear substitution products (Scheme 1). In a very few cases, good levels of both regio- and enantioselectivity have been obtained with special ligands[2] or substrates.[3]

Complexes of almost all other transition metals (Mo,[4] W,[5] Fe,[6] Ru,[7] Rh,[8] Ni,[9] Cu[10]) have been probed as catalysts for asymmetric allylic substitutions. While catalysts of all these transition metals have merits in certain aspects, only Ir complexes display similar generality as Pd catalysts with respect to the scope of allylic substrates and nucleophiles. Ir catalysts have been demonstrated to be highly efficient in regio- and enantioselective allylic substitution reactions according to Scheme 1. Subsequent to the first reports of Ir-catalyzed allylic alkylations and an enantioselective version in 1997,[11,12] the reaction has been developed with respect to both catalyst quality and substrate scope.[13] Extensive mechanistic studies[14,15] have led to the identification of the active catalysts and procedures for the preparation of the intermediary (π-allyl)Ir complexes. The usually high regio- and enantioselectivity with predictable product configuration make the Ir-catalyzed allylic substitution attractive for organic synthesis.

Scheme 1. Transition Metal (TM)-Catalyzed Allylic Substitutions of Monosubstituted Allyl Derivatives



With respect to nucleophiles, the reaction is particularly broad in scope. In addition to soft carbon nucleophiles whose conjugate acids have pK_a < 25, direct allylic arylation[16] and dearomatization[17] reactions have been accomplished, and even arylzinc reagents[18] have been successfully used.

The direct use of alkenes as nucleophiles was not known until 2009, when we serendipitously discovered an Ir-catalyzed vinylation of allylic carbonates with *o*-aminostyrene derivatives (Scheme 2, A)[19] in our ongoing program of studying Ir-catalyzed allylic substitution reactions.[20] When a domino allylic vinylation/amination strategy was employed, 2,3-dihydro-1*H*-benzo[*b*]azapines could be successfully obtained in excellent yields and enantioselectivities (Scheme 2, B).[21] It was originally intended to provide a synthesis of enantioenriched

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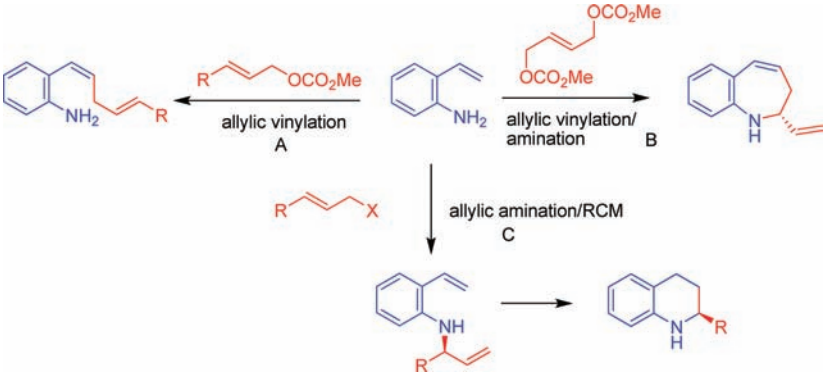
Scheme 2. Ir-Catalyzed Allylic Vinylation, Domino Allylic Vinylation/Amination, and Allylic Amination Reactions



tetrahydroquinolines, which are common among biologically interesting natural products and pharmaceuticals,[22] via an asymmetric allylic amination[23] and ring-closing metathesis (RCM) sequence (Scheme 2, C). This reaction could not be accomplished with the commonly used allylic carbonates as substrates (X = OCO_2R').

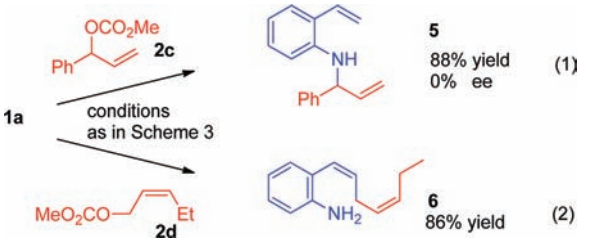
Mechanistic studies of the allylic vinylation reaction with *o*-aminostyrene derivatives revealed that the leaving group of the allyl precursor plays a key role in determining the chemoselectivity between the allylic vinylation reaction and the allylic amination reaction. With allyl diethyl phosphates as substrates [Scheme 2, X = $OPO(OEt)_2$], the Ir-catalyzed allylic substitution proceeds via an allylic amination pathway (Scheme 2, C). Subsequent RCM and catalytic hydrogenation leads to highly enantioenriched tetrahydroquinolines, in particular (−)-angustureine.[24]

Here we report a full account of our work on the Ir-catalyzed allylic substitution reactions with *o*-aminostyrene derivatives, including the allylic vinylation, the allylic vinylation/asymmetric allylic amination domino reaction, and the asymmetric allylic amination, as well as mechanistic studies and applications of these methods.

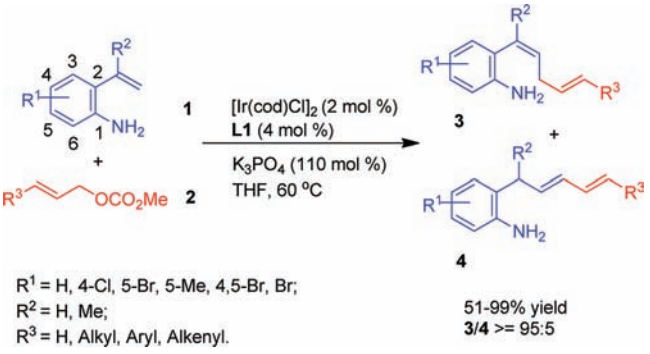
RESULTS AND DISCUSSION

Iridium-Catalyzed Allylic Vinylation Reaction with *o*-Aminostyrene Derivatives. First, the Ir-catalyzed reaction of 2-aminostyrene (**1a**) with (*E*)-3-(4-methoxyphenyl)allyl methyl carbonate (**2a**) was investigated with respect to the influence of the ligand (Table 1). The new double bond was formed highly selectively in a *cis* configuration, as confirmed by X-ray and NMR analysis. While phosphoramidite ligands promoted the reaction, PPh_3, $P(OPh)_3$, and dppe failed to afford the allylic vinylation products.

Under the optimized conditions (Scheme 3), 29 combinations of *o*-aminostyrenes and allylic carbonates were successfully investigated.[19] In some cases with R^3 = Ar, byproduct **4**



Scheme 3. Substrate Scope of the Ir-Catalyzed Allylic Vinylation Reaction



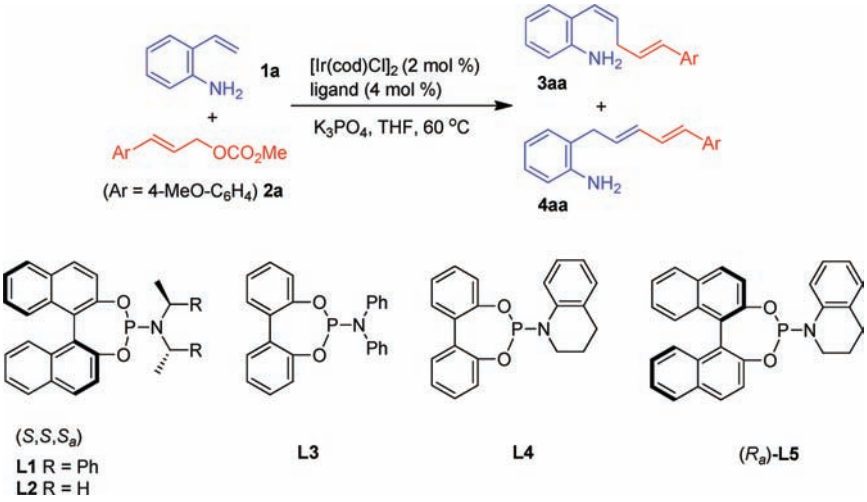
was formed in a maximum yield of 5% by isomerization of **3**, especially with prolonged reaction times and use of strong base. Carbonate substrates derived from γ-alkyl allyl alcohols afforded allylic vinylation products without isomerized product **4**.

Interestingly, under the same catalytic conditions, the reaction of **1a** with **2c** led to allylic amination product **5** in 88% yield, but without induction of enantioselectivity (eq 1). The reaction of **1a** with **2d** afforded (*Z*,*Z*)-diene **6** in 86% yield, maintaining the *Z* geometry of the double bond in the allylic substrate (eq 2).[25]

Iridium-Catalyzed Domino Allylic Vinylation/Amination Reaction. During the study of the allylic vinylation reaction, we noticed that allylic amination reaction took place after the allylic vinylation reaction when an excess of allyl carbonate was used and a prolonged reaction time was applied. This clearly indicated that the Ir complex could catalyze both types of reactions, the allylic vinylation and the allylic amination, in the same flask. The allylic amination product **7** was obtained in 57% yield with good enantioselectivity (86% ee) (eq 3).

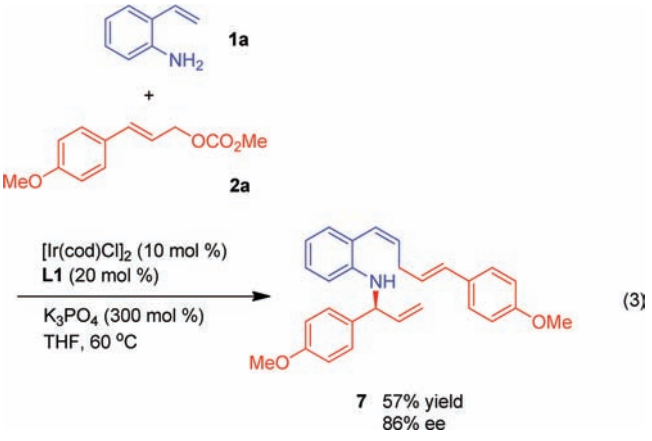
Inspired by this result, we devised an Ir-catalyzed domino allylic vinylation/intramolecular allylic amination reaction by utilizing (*E*)-but-2-ene-1,4-diyl dimethyl dicarbonate as the substrate, in which two reactive allylic sites are present (Scheme 4). Notably, the resultant 1-benzazepine moiety constitutes the core structure of numerous pharmacologically important compounds.[26] Several members of this class have exhibited biological activity toward various targets such as

Table 1. Screening of Various Ligands in an Ir-Catalyzed Allylic Vinylation Reaction[a]

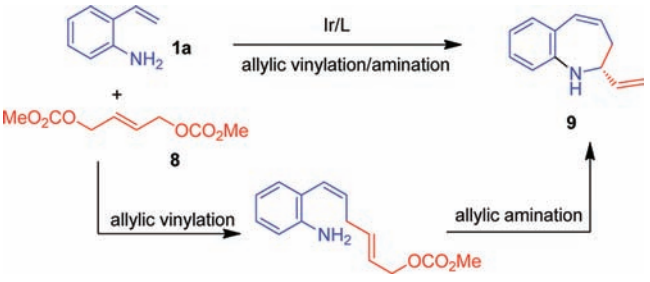


entry	ligand	time (h)	% conv.[c] (% yield[b])	3aa/4aa[c]
1	**L1**	2	>95 (87)	95:5
2	**L2**	12	–	–
3	**L3**	24	20 (16)	90:10
4	**L4**	24	50 (27)	98:2
5	**L5**	24	85 (71)	98:2
6	PPh_3	12	–	–
7	$P(OPh)_3$	12	–	–
8	dppe	12	–	–

[a] Reaction conditions: 0.004 mmol of $[Ir(cod)Cl]_2$, 0.008 mmol of ligand, 0.2 mmol of **1a**, 0.22 mmol of **2a**, and 0.22 mmol of K_3PO_4 in 2 mL of THF. The catalyst was prepared via *n*-$PrNH_2$ activation. [b] Isolated yields. [c] Determined by ^1H NMR analysis of the crude reaction mixture.



Scheme 4. Domino Reaction for the Synthesis of 1-Benzazepine Derivatives

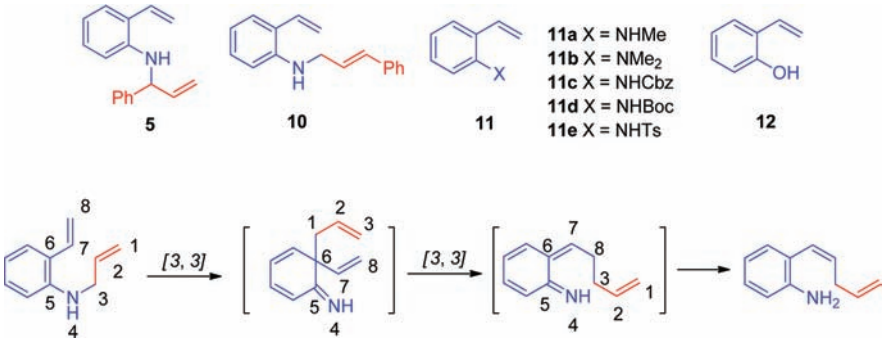


enzymes, ion channels, and G-protein-coupled receptors (GPCRs).[27,28] Despite their interesting biological activities, 1-benzazepine derivatives have received little synthetic attention.[29,30] Therefore, an efficient catalytic asymmetric synthesis of 1-benzazepine derivatives is highly desirable.

After tuning of the reaction conditions [4 mol % $[Ir(cod)Cl]_2$, 8 mol % **L1**, and 2.6 equiv of DABCO in THF at 50 °C], the domino allylic vinylation/allylic amination reaction between *o*-aminostyrenes and (*E*)-but-2-ene-1,4-diyl dimethyl dicarbonate was realized.[21] The reaction was carried out with 13 examples, including *o*-aminostyrenes with electron-donating or -accepting substituents on the aryl group and a methyl substituent at C1 of the vinyl group. Yields with electron-donating groups were excellent, while those with electron-withdrawing groups were not satisfactory. In all cases, excellent ee's were obtained.

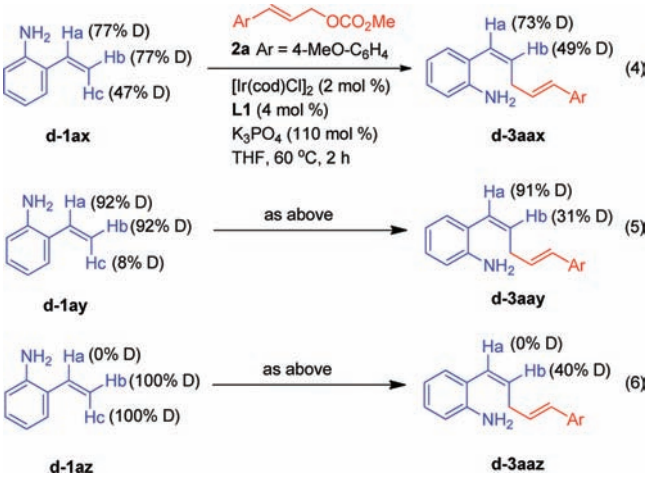
Mechanistic Studies of the Ir-Catalyzed Allylic Vinylation Reaction. The unique chemoselectivity in the Ir-catalyzed allylic substitution reaction of *o*-aminostyrenes prompted us to investigate the reaction mechanism. First, formation of the products via double [3,3] sigmatropic rearrangements of the allylic amination product was considered as possibility (Scheme 5). In order to test this hypothesis, the amination products **5** and **10** were synthesized and tested

Scheme 5. Hypothesis of Vinylation Product Formation via Double [3,3] Sigmatropic Rearrangements

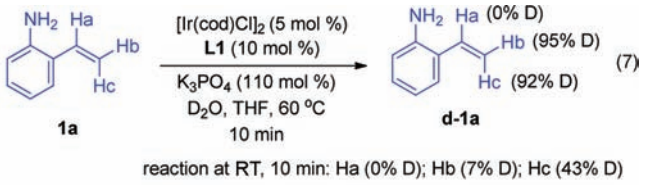


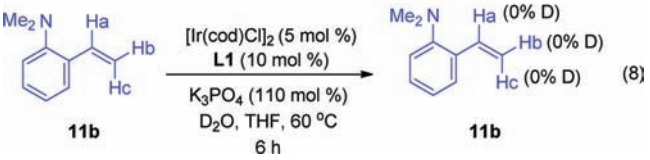
under the optimized conditions. The fact that no vinylation product was observed suggests that a reaction through double [3,3] sigmatropic rearrangements is less likely. No reaction occurred when styrene or **11a**−**c** were used, while allylic amination or etherification reactions proceeded with substrates **11d**, **11e**, and **12** (X = NHBoc, NHTs, OH).

We next synthesized several deuterated derivatives of **1a** with various deuteration ratios of the olefinic hydrogens (eqs 4−6). All of these compounds were then subjected to the optimized allylic vinylation reaction conditions. In the vinylation products, the deuterium content in the internal vinylic position Ha was maintained. However, the deuterium content in the external vinylic position Hb decreased to some extent in all cases (77 to 49% in eq 4, 92 to 31% in eq 5, and 100 to 40% in eq 6).



To rationalize the H/D exchange of the olefinic hydrogens in *o*-aminostyrene substrates, the following experiments were carried out. Treatment of **1a** with a catalytic amount (10 mol %) of Ir/**L1** in the presence of K_3PO_4 and D_2O at 60 °C (eq 7) led to the incorporation of deuterium in recovered **1a**. The terminal vinylic Hb and Hc were both deuterated to a high extent (95 and 92%, respectively). A control experiment confirmed that no deuteration was incorporated at position Hb or Hc in the absence of the Ir/**L1** catalyst. These results suggest that the vinylation reaction proceeds via steps in which the H/D exchange might occur for terminal vinylic hydrogens but not the internal vinylic hydrogen. When the reaction was carried out at room temperature (RT) for 10 min, more D incorporation was found at Hc (43%) than at Hb (7%), which is in accord with the existence of a *cis*-vinyl carbon−Ir bond. When an unreactive substrate, *N*,*N*-dimethyl-2-vinylaniline (**11b**), was treated under otherwise identical reaction conditions, no deuteration was found at any of the olefinic positions (eq 8).





We next tried to answer the question of whether the allylic vinylation reaction proceeds via the (π-allyl)Ir complex generated from allyllic carbonates and a cyclometalated Ir catalyst (eq 9). The (π-allyl)Ir complexes **13** and **15** were synthesized according to the reported procedure.[15f] When **13** was treated with **1a** and Cs_2CO_3 in THF at RT, allylic amination product **14** was obtained exclusively, and no allylic vinylation product was observed. Similarly, when the (π-allyl)Ir complex **15** derived from *p*-methoxycinnamyl methyl carbonate was used, the allylic amination products were also found as the major products (**16**/**3aa** = 5/1; eq 10). These results suggest that the preformed (π-allyl)Ir complex is not the dominant intermediate during the allylic vinylation process. On the other hand, the predominant formation of the allylic amination products indicates that the allylic amination reaction might be possible with *o*-aminostyrenes by using allylic precursors more reactive than carbonates in order to facilitate the formation of the (π-allyl)Ir intermediates.

On the basis of the above experimental results, a working model for the Ir-catalyzed allylic vinylation reaction is proposed (Scheme 6). The coordination of 2-vinylaniline to the cyclometalated iridium complex **A**[14a] yields complex **B** with the amino group and the coordinated vinyl group in close proximity. A base facilitates deprotonation of complex **B** after which an intramolecular rearrangement generates the unstable dearomatization complex **C** with a newly formed C−Ir bond. This potentially

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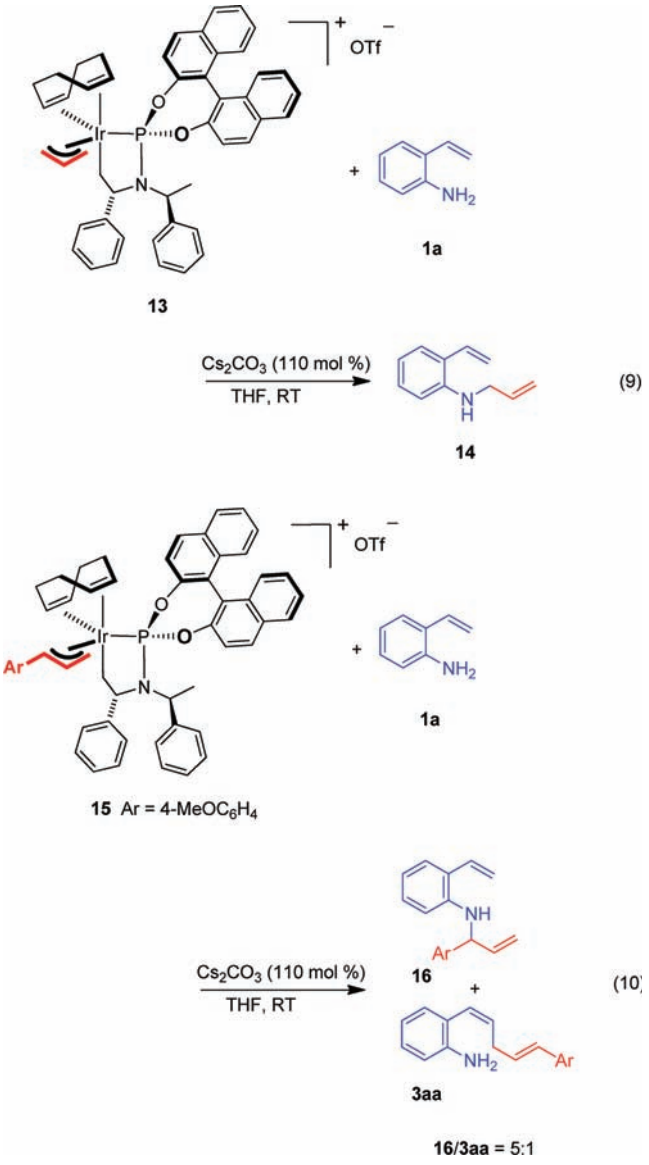
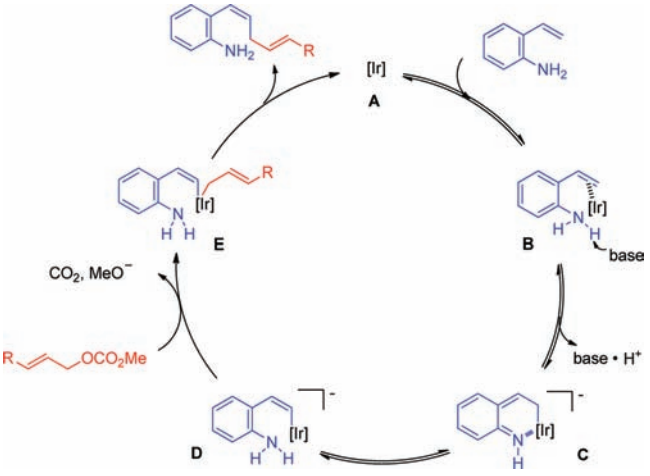


reversible step is likely responsible for the H/D exchange observed for the olefinic hydrogens in the deuteration experiments described above. Aromatization of **C** gives complex **D** with a *cis* double bond. Complex **D** then undergoes oxidative addition of allyl methyl carbonate, generating complex **E** after a subsequent release of CO_2. Finally, reductive elimination yields the allylic vinylation product and regenerates the active iridium catalyst to complete the catalytic cycle.

Ir-Catalyzed Enantioselective Allylic Amination Reaction with *o*-Aminostyrene Derivatives. After the allylic vinylation reaction and allylic vinylation/amination domino reaction were realized, the enantioselective allylic amination reaction with *o*-aminostyrene derivatives was attempted. We followed a clue obtained during the course of the mechanistic investigation of the allylic vinylation reaction: the stoichiometric reaction between the preformed (π-allyl)Ir complex and 2-vinylaniline leads predominantly to allylic amination products. This suggested that the reaction pathway might be tunable by variation of the leaving group of the allylic precursor.

At the outset, we examined several leaving groups of the allylic precursors, using cinnamyl acetate (**17**), cinnamyl *tert*-butyl carbonate (**18**), cinnamyl methyl carbonate (**2b**), and

Scheme 6. Proposed Working Model of the Ir-Catalyzed Allylic Vinylation Reaction



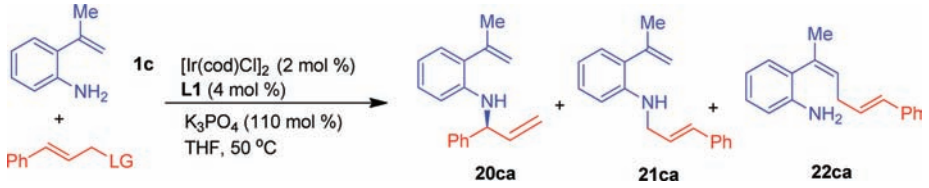
cinnamyl diethyl phosphate (**19a**) as substrates. The results are summarized in Table 2. The allylic amination pathway was completely inhibited when **17** was used, and only the allylic vinylation product was obtained in 53% yield (entry 1). However, the allylic amination products were formed to some degree when **18** or **2b** was employed, although the allylic vinylation pathway predominated (entries 2 and 3). When **19a** was used, the allylic amination product was formed in 61% yield with 77% ee. In addition, a small amount of allylic vinylation product was formed (entry 4).

Further screening of ligands did not give satisfactory results in terms of chemo-, regio-, and enantioselectivity (Table 3, entries 1−8). Fortunately, with the catalyst derived from $[Ir(dbcot)Cl]_2$ (dbcot = dibenzo[*a*,*e*]cyclooctatetraene)/**L7**, introduced by Helmchen and co-workers in 2008,[23g] the reaction of **19a** with *o*-vinylaniline **1c** afforded the allylic amination product in excellent yield (89%) and enantioselectivity (92% ee) (entry 9).

Further tuning of the reaction parameters (ligand, base, solvent, temperature) led to the optimized reaction conditions (i.e., 2 mol % $[Ir(dbcot)Cl]_2$, 4 mol % **L7**, and 110 mol % K_3PO_4 in THF or dioxane at 50 °C). Under the optimal conditions, the substrate scope was examined with various *o*-aminostyrenes and allylic diethyl phosphates. The results are summarized in Table 4. Reactions between cinnamyl phosphates substituted on the aryl group (entries 2−4) and 2-vinylaniline all led to the corresponding allylic amination products with excellent yields (80−95%) and ees (85−91%). Not only arylallyl phosphates but also *n*-pentyl-substituted allylic phosphate **19e** underwent the allylic amination smoothly (91% yield, 84% ee; entry 5). Notably, the corresponding allylic amination product is a key intermediate in the previously proposed synthetic route to the alkaloid angustureine. In addition, *o*-aminostyrenes bearing electron-donating groups (entries 6 and 11) or electron-withdrawing groups (entries 9 and 10) were well-tolerated under the optimized reaction conditions. Finally, no reaction occurred when dibromide-bearing vinylaniline **1g** was used (entry 12).

1,2-Dihydroquinoline is a structural motif in numerous natural and unnatural products with interesting bioactivity.[31] To demonstrate the utility of the above Ir-catalyzed enantioselective allylic amination reaction with *o*-aminostyrenes, the

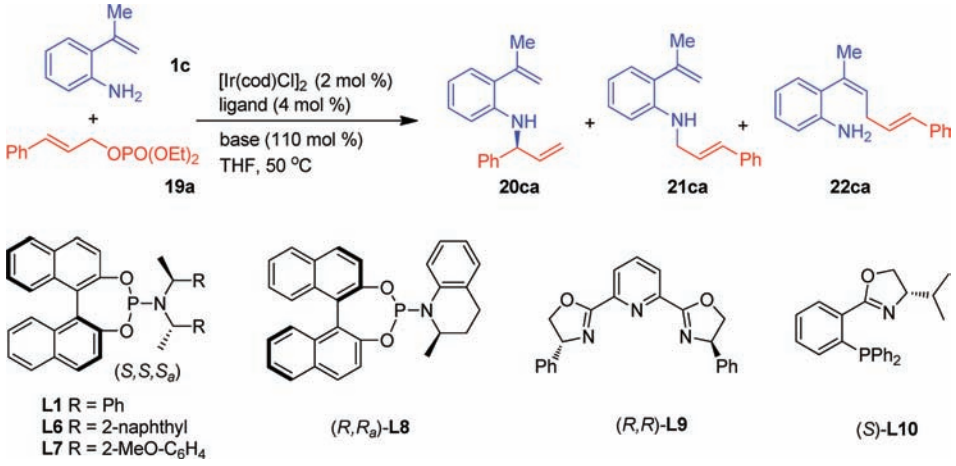
Table 2. Examination of Several Leaving Groups (LGs) of Allylic Precursors[a]



entry	LG	(20ca + 21ca)/22ca[b]	% yield of 20ca + 21ca[c]	% ee[d]	% yield of 22ca[c]
1	OAc (**17**)	<1/99	–	–	53
2	OBoc (**18**)	7/93	–	–	63
3	OCO_2Me (**2b**)	15/85	–	–	65
4	$OPO(OEt)_2$ (**19a**)	72/28	61	77	–

[a] Reaction conditions: 0.004 mmol of $[Ir(cod)Cl]_2$, 0.008 mmol of **L1**, 0.2 mmol of **1c**, 0.2 mmol of allylic precursor, and 0.22 mmol of K_3PO_4 in THF (2 mL); the catalyst was prepared via *n*-$PrNH_2$ activation. [b] Determined by ^1H NMR analysis of the crude reaction mixture. [c] Isolated yields. [d] Determined by HPLC analysis.

Table 3. Screening of Various Chiral Ligands[a]



entry	ligand	base	temp (°C)	% yield of 20ca + 21ca[b]	20ca/21ca/22ca[c]	% ee[d]
1	**L1**	K_3PO_4	50	61	71/1/28	77
2	**L1**	DABCO	50	37	56/1/43	67
3	**L1**	K_3PO_4	RT	87	85/2/13	74
4	**L6**	K_3PO_4	RT	89	93/2/5	64
5	**L7**	K_3PO_4	RT	47	54/1/45	42
6	**L8**	K_3PO_4	RT	95	63/37/0	71
7	**L9**	K_3PO_4	RT	–	–	–
8	**L10**	K_3PO_4	RT	–	–	–
9[e]	**L7**	K_3PO_4	50	89	97/1/2	92

[a] Reaction conditions: 0.004 mmol of $[Ir(cod)Cl]_2$, 0.008 mmol of ligand, 0.2 mmol of **1c**, 0.2 mmol of **19a**, and 0.22 mmol of base in THF (2 mL); the catalyst was prepared via *n*-$PrNH_2$ activation. [b] Isolated yields. [c] Determined by ^1H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis. [e] 0.004 mmol of $[Ir(dbcot)Cl]_2$ was used instead of $[Ir(cod)Cl]_2$.

amination products were transformed into substituted 1,2-dihydroquinolines. This was achieved in a two-step process including protection with trifluoroacetic anhydride and then an RCM reaction with **Zhan-1B** as the catalyst (2 mol %). The results are summarized in Table 5. In general, the 1,2-dihydroquinolines were obtained in good yields without notable loss of enantiomeric purity.

With this procedure in hand, the synthesis of (−)-angustureine (**25**) was carried out as outlined in Scheme 7. Hydrogenation of 1,2-dihydroquinoline **23ae** with 10 mol % Pd/C as the catalyst and subsequent deprotection of the trifluoroacetyl group produced 2-pentyl-1,2,3,4-tetrahydroquinoline (**24**) in excellent yield (94%). Methylation of **24** with MeI afforded **25** in 85% yield. Its

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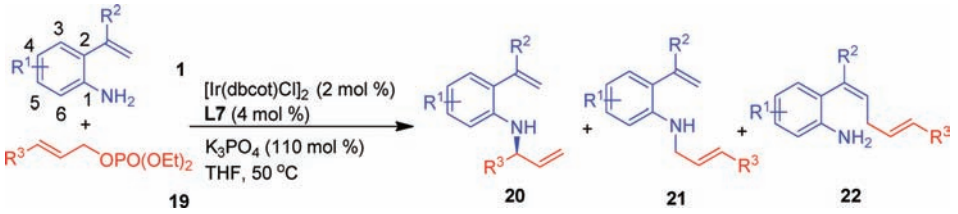
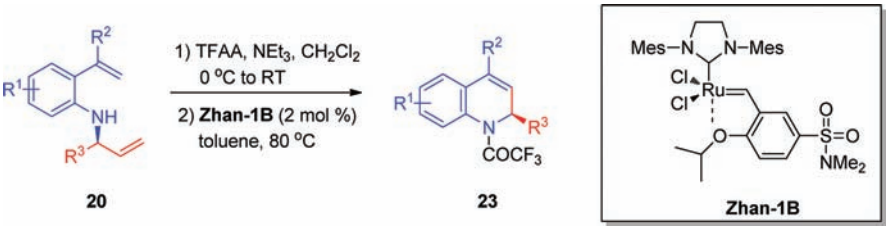
Table 4. Substrate Scope of Ir-Catalyzed Allylic Amination[a]



entry	**1**; R^1, R^2	**19**, R^3	solvent	% yield of **20** + **21**[b]	**20**/**21**/**22**[c]	**20**, % ee[d]
1	**1a**; H, H	**19a**, Ph	dioxane	82	94/1/5	**20aa**, 93
2	**1a**; H, H	**19b**, 3-ClC_6H_4	THF	95	98/1/1	**20ab**, 89
3	**1a**; H, H	**19c**, 4-BrC_6H_4	THF	88	94/1/5	**20ac**, 91
4	**1a**; H, H	**19d**, 4-$CF_3C_6H_4$	THF	80	92/1/7	**20ad**, 85
5	**1a**; H, H	**19e**, *n*-C_5H_{11}	THF	91	98/1/1	**20ae**, 84
6	**1b**; 5-Me, H	**19a**, Ph	dioxane	91	94/1/5	**20ba**, 93
7	**1c**; H, Me	**19a**, Ph	THF	89	97/1/2	**20ca**, 92
8	**1c**; H, Me	**19b**, 3-ClC_6H_4	THF	89	92/1/7	**20cb**, 89
9	**1d**; 4-Br, Me	**19a**, Ph	dioxane	86	94/1/5	**20da**, 92
10	**1e**; 5-Cl, Me	**19a**, Ph	THF	91	93/2/5	**20ea**, 92
11	**1f**; 4-Me, H	**19a**, Ph	dioxane	91	98/1/1	**20fa**, 92
12	**1g**; 4,6-Br_2, H	**19a**, Ph	dioxane	–	–	–

[a] Reaction conditions: 0.004 mmol of $[Ir(dbcot)Cl]_2$, 0.008 mmol of **L7**, 0.2 mmol of **1**, 0.2 mmol of **19**, and 0.22 mmol of K_3PO_4 in 2 mL of THF or dioxane; the catalyst was prepared via *n*-$PrNH_2$ activation. [b] Isolated yields. [c] Determined by ^1H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis.

Table 5. Trifluoroacetyl Protection and RCM Reaction of 20[a]

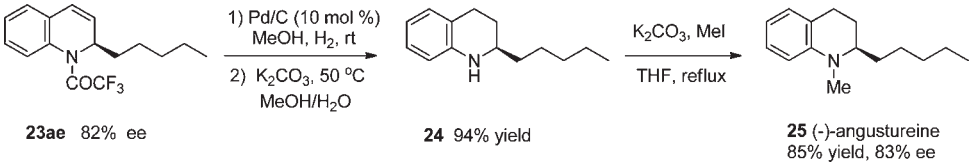


entry	**20**; R^1, R^2, R^3	time (h)	temp (°C)	**23**, % yield[b]	% ee[c,d]
1	**20aa**; H, H, Ph	12	80	**23aa**, 93	90 (93)
2	**20ab**; H, H, 3-ClC_6H_4	12	80	**23ab**, 84	88 (89)
3	**20ac**; H, H, 4-BrC_6H_4	12	80	**23ac**, 88	88 (91)
4	**20ad**; H, H, 4-$CF_3C_6H_4$	12	80	**23ad**, 82	81 (85)
5	**20ae**; H, H, *n*-C_5H_{11}	12	80	**23ae**, 87	82 (84)
6	**20ca**; H, Me, Ph	24	reflux	**23ca**, 83	92 (92)
7	**20cb**; H, Me, 3-ClC_6H_4	24	reflux	**23cb**, 71	91 (89)
8	**20da**; 4-Br, Me, Ph	24	reflux	**23da**, 79	92 (92)
9	**20ea**; 5-Cl, Me, Ph	24	reflux	**23ea**, 64	93 (92)
10	**20fa**; 4-Me, H, Ph	12	80	**23fa**, 95	91 (92)

[a] Reaction conditions: (1) 0.2 mmol of **20**, 0.3 mmol of TFAA, and 0.4 mmol of NEt_3 in 2 mL of CH_2Cl_2 at 0 °C; (2) 0.004 mmol of **Zhan-1B** in 2 mL of toluene. [b] Isolated yields. [c] Determined by HPLC analysis. [d] The ee's of **20** are given in parentheses.

absolute configuration was assigned to be *R* by comparison with the optical rotation value recorded.[32] Starting from the 2-vinylaniline, (−)-angustureine **25** was synthesized in six steps in 64% overall yield. Thus, the new route provides a general strategy for construction of di- and tetrahydroquinoline-based natural products and analogues. Notably, Evans and co-workers for the first time introduced the asymmetric allylic amination/RCM strategy to construct the enantiomerically enriched dihydroquinolines.[33]

Scheme 7. Total Synthesis of (−)-Angustureine (25)



23ae 82% ee

24 94% yield

25 (-)-angustureine
85% yield, 83% ee

In addition, **25** was also synthesized by Nishida and co-workers utilizing Mitsunobu amination of an enantiopure allylic alcohol followed by an RCM reaction.[24g]

■ CONCLUSION

With *o*-aminostyrenes as the nucleophiles, we have successfully developed an Ir-catalyzed allylic vinylation reaction, a domino allylic vinylation/asymmetric intramolecular allylic amination reaction, and an asymmetric allylic amination reaction. The Ir-catalyzed allylic vinylation reaction with *o*-aminostyrenes and allylic carbonates provides skipped (*Z*,*E*)-dienes. Employing (*E*)-but-2-ene-diyl dimethyl dicarbonate as the electrophile led to the realization of the Ir-catalyzed domino allylic vinylation/amination reaction, which affords 2,3-dihydro-1*H*-benzo[*b*]azepines with high enantioselectivity. Inspired by mechanistic studies, we realized an enantioselective allylic amination reaction with *o*-aminostyrenes by using allylic diethyl phosphates as the allyl precursors. The allylic amination products were readily transformed into enantioenriched substituted 1,2-dihydroquinolines by a subsequent RCM reaction. The utility of this route was further demonstrated by a total synthesis of (−)-angustureine.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and analysis data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
slyou@sioc.ac.cn

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